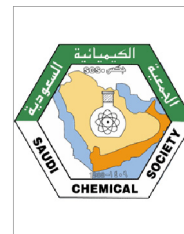




King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Comparison between polyvinyl alcohol (PVA) nanofiber and polyvinyl alcohol (PVA) nanofiber/hydroxyapatite (HA) for removal of Zn^{2+} ions from wastewater

A.M. Abd El-aziz ^a, Azza El-Maghraby ^{a,*}, Nahla A. Taha ^{a,b}

^a Department of Fabrication Technology, Advanced Technology and New Materials Research Institute, City for Scientific Research and Technology Applications, Alexandria 23713, Egypt

^b Chemistry Department, Al-lith University College, Umm Al-Qura University, Saudi Arabia

Received 4 July 2016; accepted 26 September 2016

KEYWORDS

Nanofibers;
Electrospinning;
Polyvinyl alcohol;
Hydroxyapatite;
Water treatment;
 Zn^{2+} removal

Abstract Nanocomposites in the form of continuous and aligned polyvinyl alcohol (PVA) nanofibers have been obtained by the electrospinning process. These fibers were used as matrix for hydroxyapatite (HA). PVA and PVA/HA nanofibers were fabricated and crosslinked with glutaraldehyde (GA). The hybrid of polymer with ceramics (HA) shows good properties of large surface area and good porosity that were demonstrated by different characterization techniques such as FTIR, SEM, XRD and EDX which illustrate the ratio of HA. The prepared nanofibrous membranes are used for removal of Zn^{2+} from simulated water. The potential of these synthesized sorbents to remove Zn^{2+} ions from aqueous solutions was investigated in batch experiments, where several parameters such as the sorbate/sorbent's contact time, initial Zn^{2+} ions concentration and sorbent dosage were investigated. The equilibrium concentration of Zn^{2+} ions was identified by the atomic absorption spectrophotometry and the adsorption process was studied by the isotherm models such as Langmuir, Freundlich and Temkin. The Zn^{2+} adsorption process for PVA and PVA/HA nanofibrous membranes was fitted to Langmuir and Freundlich isotherm models respectively.

© 2016 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

* Corresponding author.

E-mail address: maghrabyazza@yahoo.com (A. El-Maghraby).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

1. Introduction

Nowadays, pollution of water from the contamination of heavy metals is a severe environmental problem. Metals such as chromium, copper, iron, lead, silver, and zinc, which have high toxic and non-biodegradable properties, can cause problems to both the environment and the living organisms with extremely high levels (Abdouss et al., 2012; Freitas et al., 2008; Badmus et al., 2007). Many methods (such

<http://dx.doi.org/10.1016/j.arabjc.2016.09.025>

1878-5352 © 2016 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Please cite this article in press as: Abd El-aziz, A.M. et al., Comparison between polyvinyl alcohol (PVA) nanofiber and polyvinyl alcohol (PVA) nanofiber/hydroxyapatite (HA) for removal of Zn^{2+} ions from wastewater. Arabian Journal of Chemistry (2016), <http://dx.doi.org/10.1016/j.arabjc.2016.09.025>

as adsorption, electroplating, ion exchange, membrane separation and precipitation) are being used to remove the ions of these metals from aqueous effluents. Among these, adsorption is commonly regarded as an effective and economical method for wastewater treatment (Illinois, n.d.).

Nano-scale materials can be designed to exhibit novel improvement of the physical and chemical properties and are designed to become a discipline as important as polymers are in chemistry (Kampalananwat and Supaphol, 2010). More than 100 polymers, both synthetic and natural, have been successfully electrospun into nanofibers. Mostly from polymer solutions any polymers may be electrospun into nanofibers, provided that the polymer molecular weight is sufficiently high and the solvent can be evaporated in time during the jet transit period over a distance between the spinneret and the collector (Feng et al., 2013).

PVA is a synthetic water-soluble hydrophilic polymer. The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis. It has been widely used in adhesives, emulsifiers, the textile and paper industry applications and in the attainment of amphiphilic membranes for enzyme immobilization where properties can be improved, such as mechanical, thermal and chemical stability. Applications of PVA are limited by its hydrophilicity, but chemical cross-linking improves its stability in aqueous media. Chemical cross-linking by glutaraldehyde (GA), a dialdehyde, during which the hydroxyl groups of the PVA and the aldehyde groups of GA react in the presence of a strong acid, has been well studied. Membranes of nanofibrous cross-linked PVA are being studied in filtration and membrane applications. Cross-linking is advantageous because it renders the nanofibers insoluble in all solvents and increases the mechanical properties of the membranes; insolubility is especially desirable for filtration applications.

A novel class of materials called organic-inorganic hybrids would combine properties of organic polymers with ceramics such as hydroxyapatite (HA). Hybrids would combine properties of organic polymers with ceramics. These different components can be mixed at length scales ranging from nanometer to micrometer, in virtually any ratio leading to the so-called hybrid organic-inorganic materials (Fonseca et al., 2006). Hydroxyapatite is an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability, and low cost. It was conducted in adsorption of a wide variety of metals (e.g., Cr, Co, Cu, Cd, Zn, Ni, Pu, Pb, As, Sb, U, and V). The sorption takes place through ionic exchange reaction, surface complexation with phosphate, calcium and hydroxyl groups and/or co-precipitation of new partially soluble phases (Mobasherpour et al., 2011).

The aim of this work was to prepare and characterize the cross linked polyvinyl alcohol nanofibers and nanofibrous composite of both polyvinyl alcohol/hydroxyapatite nanofibers and compare between them by the removal of the contaminant Zn^{2+} ion from aqueous solution. The thermodynamics of this adsorption process of Zn^{2+} from the simulated water have been studied by three isotherm models such as Langmuir, Freundlich and Temkin.

2. Materials and methods

2.1. Materials

Polyvinyl alcohol “Mwt = 72.000 g/mol”, Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) (98%) and Phosphoric acid, (H_3PO_4) (85%) were obtained from Sigma Aldrich. Glutaraldehyde 25% aq. Solution was purchased from Alfa Aesar, “A Johnson Matthey Company”. Zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$, $M = 297.48$ g/mol, was obtained from Fluka. All chemicals were used without further purification.

2.2. Methods

2.2.1. Preparation of hydroxyapatite (HA)

The HA Powder was synthesized by the co-precipitation process of 1:2 Molar ratio of $Ca(NO_3)_2 \cdot 4H_2O$ and H_3PO_4 of the same volume. The HA particles were precipitated upon the addition of NH_4OH till pH equal to 10. After the precipitation the solution was aged in a water bath for 24 h. The precipitation was filtered and then dried at $100^\circ C$ for 24 h (Scalera et al., 2013) (Fig. 1).

2.2.2. Preparation of polyvinyl alcohol (PVA) nanofibers

Different concentrations (5, 8, 10) wt% of PVA water solutions were prepared by stirring at $90^\circ C$ for 2 h. The prepared solutions of PVA solutions have been cross linked with glutaraldehyde (GA) by the addition of 0.25% glutaraldehyde for cross linking reaction by the stirring for 2 h at $60^\circ C$. The prepared solutions were electrospun to form polymeric nanofibers. The electrospinning apparatus (NANONC, Germany) consisted of high voltage supply, a syringe infusion pump and a ground electrode (an Aluminum foil on a stainless steel collector). The polymeric solutions were loaded into a plastic syringe (10 mL), and the applied voltage was “15 and 30” kV. The solution was constantly supplied using a syringe pump at a flow rate of 0.5 mL/h and the spinning distance between the needle and the ground electrode was 20 cm.

2.2.3. Preparation of cross-linked PVA nanofiber/hydroxyapatite nanocomposite

By the characterization of the polymeric nanofibers, we choose the 10 wt% of PVA water solution due to the smallest fiber diameters and the highest surface area. The hydroxyapatite (1 wt%) added to the 10% PVA water solution by the stirring for 1 h at $90^\circ C$. The addition of 0.25% GA is for cross linking reaction between the polymeric chains by the stirring for 2 h at $60^\circ C$ (Wang and Hsieh, 2010; Figueiredo et al., 2008). The

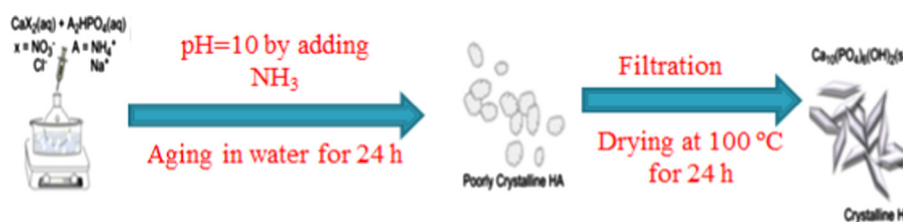


Figure 1 Mechanism of preparation of HA nanoparticle showing the two-step precipitation reaction which yields poorly crystalline HA followed by calcination of the precipitate to obtain crystalline HA nanoparticles (Mobasherpour et al., 2011).

polymeric solutions were loaded into a plastic syringe (10 mL) and allowed for electrospinning with the conditions as previously mentioned.

2.2.4. Zn^{2+} adsorption by the prepared nanofibrous membranes

The study of the adsorption of metal ions (Zn^{2+}) from an aqueous solution was investigated by the batch method. The metal ion solutions were prepared with different concentrations from 100 to 500 mg/L. Dried samples of nanofibrous membranes (PVA and PVA/HA) were used as adsorbent materials. The membranes were weighed 50 mg in aqueous solutions (100 mL) which were agitated at a constant speed of 300 rpm at room temperature (Wang and Hsieh, 2010). The concentration of Zn^{2+} ion has been determined by Atomic Absorption spectrometry (AAS).

2.2.5. Isotherms of the adsorption process

Langmuir, Freundlich and Temkin models are three isotherm models which explain the adsorption of adsorbate onto homogeneous and heterogeneous active sites of the adsorbent, respectively. Further to this, the initial concentration of metal ion Zn^{2+} was changed from 100 to 500 mg/L and the Zn^{2+} concentrations were determined by the atomic absorption spectrometry after a certain time (t). The Langmuir model of isotherm stated that "the surface catalysis is usually preceded by chemisorption, and the kinetics of surface reactions due to the monolayer adsorption" (Figueiredo et al., 2008). The model is valid for monolayer adsorption onto a surface containing a finite number of identical sites, while Temkin model considered the effects of some indirect adsorbate/adsorbent interactions on adsorption isotherms and suggested that

because of these interactions of the heat of adsorption, the molecules in the layer would decrease linearly with coverage. The form of the Langmuir isotherm can be represented by the following Equation:

$$C_e/q_e = 1/(q_m k) + (1/q_e)C_e \quad (1)$$

where q_e and q_m are the amount of the Zn^{2+} adsorbed on the membrane surface and the maximum Zn^{2+} adsorbed (mg/g). C_e is the equilibrium Zn^{2+} concentration (mg/mL) and k is the equilibrium constant.

In contrast to the homogeneous Langmuir isotherm, the Freundlich adsorption isotherm is an empirical model, which can be used for evaluating the heterogeneous binding system of Zn^{2+} onto the nanofiber surfaces.

The Freundlich equation (Eq. (2)) is expressed as

$$\ln q_e = \ln k_f + (1/n) \ln C_e \quad (2)$$

where C_e and q_e values are the equilibrium Zn^{2+} concentration (mg/mL) and the amount of the Zn^{2+} adsorbed on the membrane surface (mg/mL) respectively, while $1/n$ is the Freundlich constant that refers to the affinity of ion onto the surface of the nanofibers (Sharma and Li, 2014).

The Temkin isotherm has been used in the following form (Haider and Park, 2009):

$$q_e = RT/b * (\ln AC_e) \quad (3)$$

Eq. (3) can be expressed in its linear form as

$$q_e = B \ln A + RT/b \ln C_e \quad (4)$$

where

$$B = RT/b$$

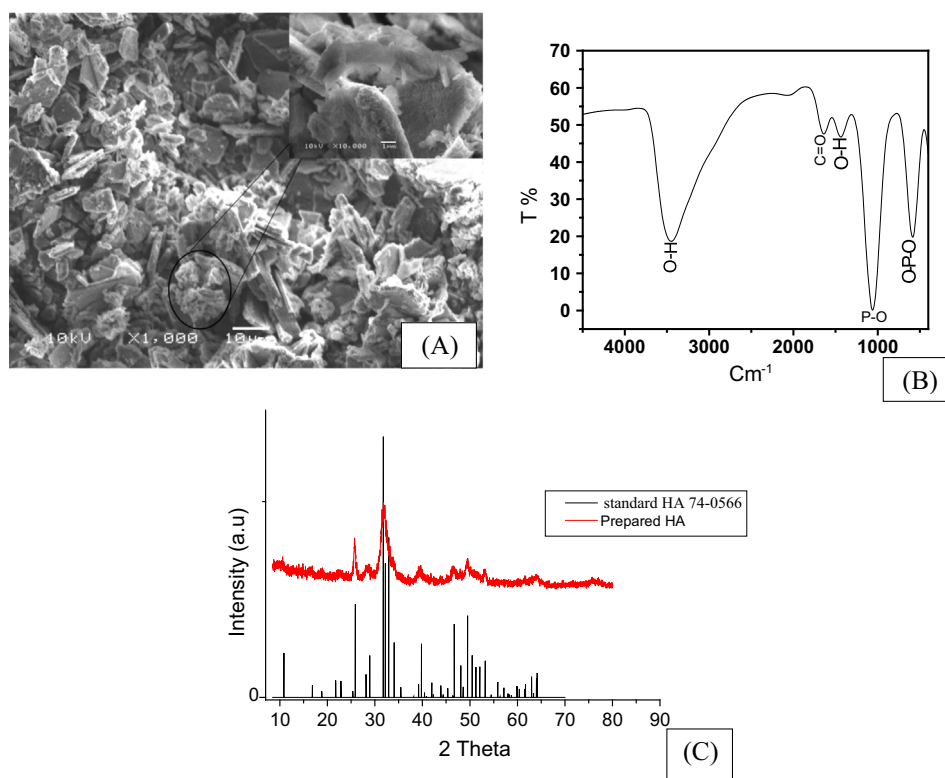


Figure 2 The characterization of the prepared hydroxyapatite: (A) SEM surface morphology, (B) FT-IR analysis and (C) XRD analysis.

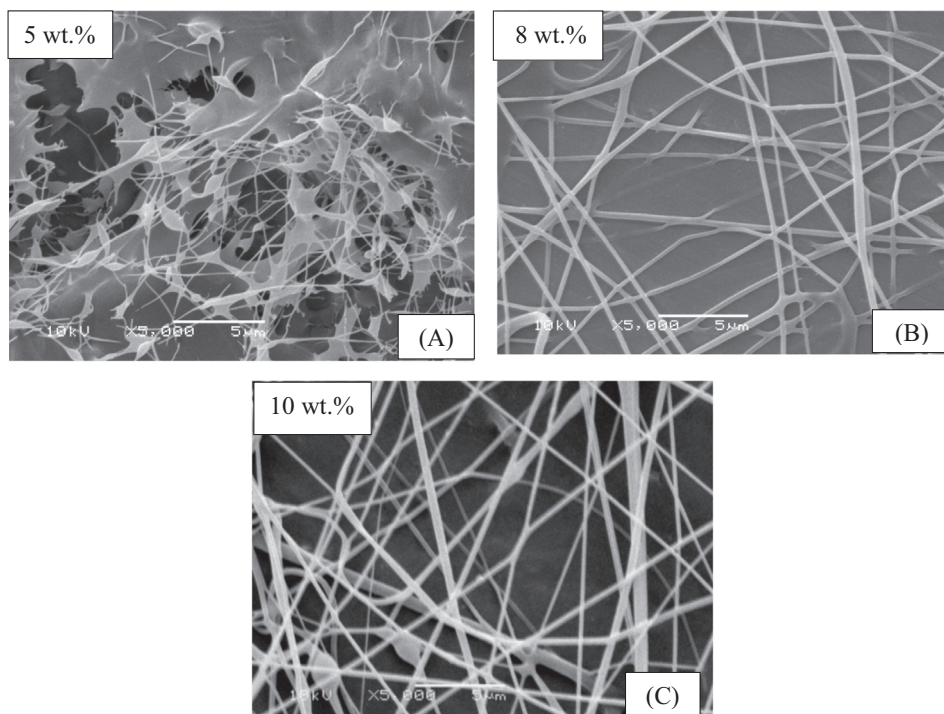


Figure 3 SEM images of PVA nanofibers with different concentrations (5, 8, 10) wt%.

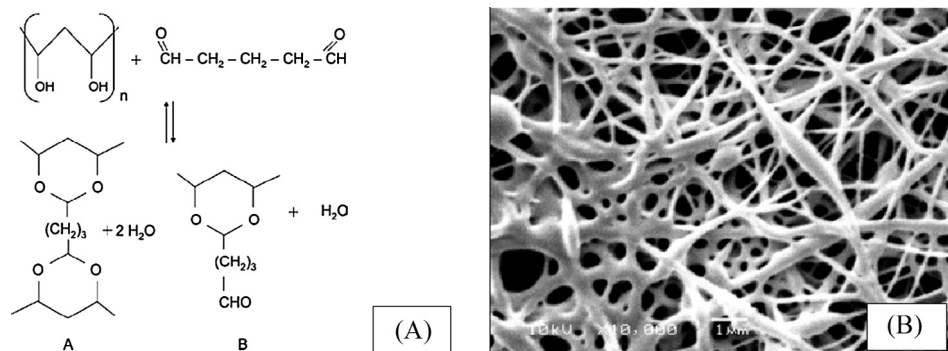


Figure 4 (A) Mechanism of the reaction between PVA and GA and (B) SEM images of 10% PVA cross-linked nanofibers.

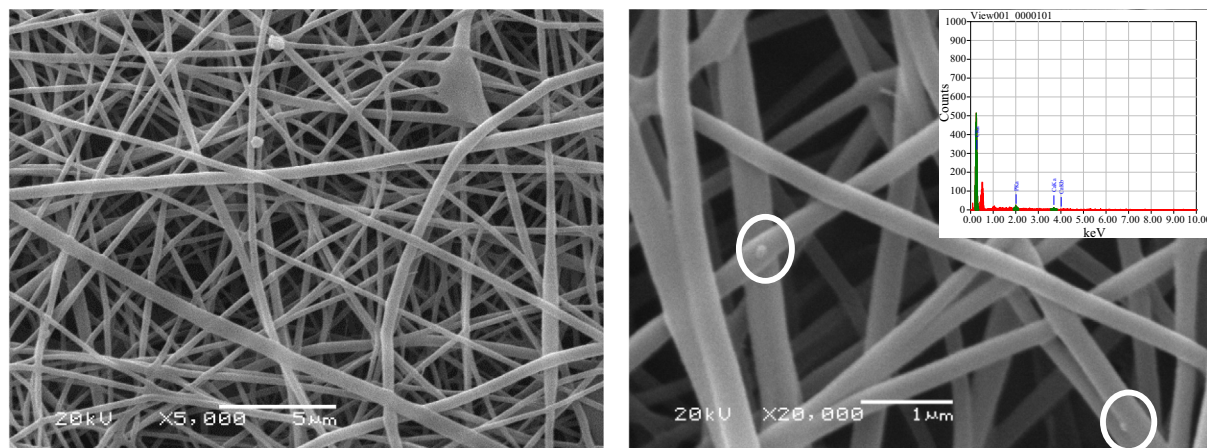


Figure 5 SEM images and EDX composition of the elements of PVA/(1%) HA nanofibers.

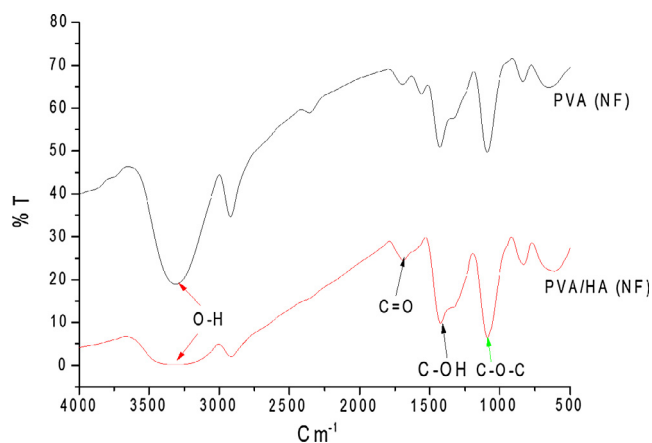


Figure 6 FT-IR of (PVA, PVA/(1%)HA) nanofibers and HA powder.

The adsorption data can be analyzed according to Eq. (4). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants A and B . The constant B is related to the heat of adsorption.

2.2.6. Characterization of the prepared materials

Fourier Transmission-IR Spectrophotometer (FTIR-8400S, Shimadzu, Japan) with a resolution of 2 cm^{-1} was used to explore the change in the functional groups before and after functionalization of the nanofibers with HA. The samples (5 mg) were milled with dry potassium bromide (KBr) (20 mg) crystals at room temperature. The spectrum was recorded in the wave number range of $4000\text{--}350\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} . To analyze the crystalline structure of the PVA powder, the electrospun (ES) PVA fiber and the ES-PVA/HA fibers, X-ray diffraction was performed using X-ray 7000 Shimadzu-Japan at room temperature. The Bragg angle (2θ) in the range from 10° to 80° was measured to determine the degree of crystallinity of the HA. The X-ray source is a Cu target generated at 30 kV and 30 mA with a scan speed 4 deg/min. The size and morphology of the electrospun fibers were investigated by the field scanning electron microscopy (SEM (JEOL JSM 6360LA, Japan), with an Electron Dispersive X-ray unit (EDX).

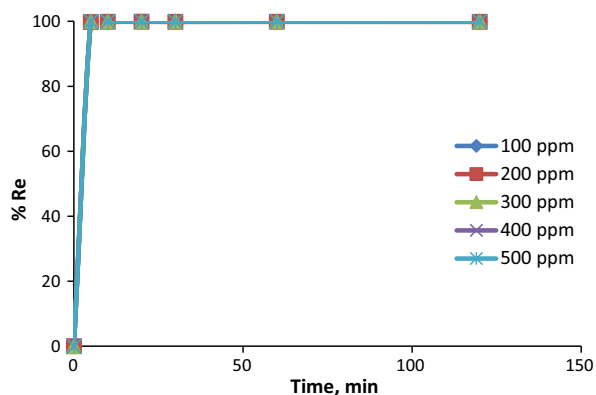


Figure 7 Effect of concentration on adsorption of Zn^{2+} by PVA (NF) (sorbent dose: 50 mg; stirring speed; 300 r.p.m; contact time: 2 h).

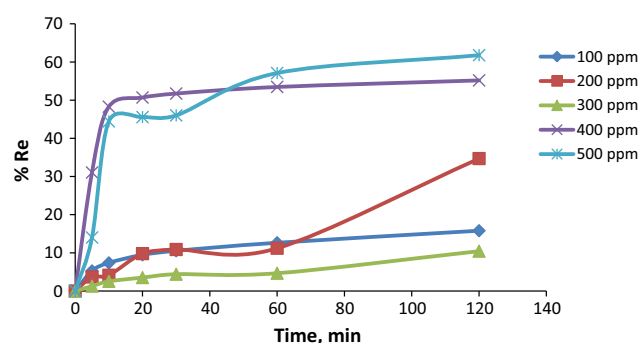


Figure 8 Effect of concentration on adsorption of Zn^{2+} by PVA/1% HA (sorbent dose: 50 mg; stirring speed; 300 rpm; contact time: 2 h).

3. Results and discussion

PVA nanofibrous membrane and PVA/HA nanocomposites were obtained by electrospinning of PVA water solution with GA and electrospinning of PVA water solution with HA in the presence of GA. The removal of Zn^{2+} from simulated water was studied.

3.1. Characterization of the prepared hydroxyapatite

The SEM micrograph, the FT-IR analysis and the XRD pattern of the porous HA templates are shown in Fig. 2A, B and C, respectively. The dense agglomerated grains of HA were observed in the SEM micrographs of the calcined HA templates. The micrographs of the clusters of HA particles have a homogenous size. The average size of the clusters was mean \pm standard deviation ($218 \pm 75\text{ nm}$) for the co-precipitation procedure of $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{H}_3\text{PO}_4]$ (Dawid, 2001).

The functional groups of the HA have been studied by the FT-IR as shown in the following. The band observed at 3417 cm^{-1} was attributed to the hydroxyl group (OH) stretching (Lan et al., 2015). The bands at 1629 cm^{-1} , 1660 cm^{-1} were attributed to V_2 bending mode of the water molecules that are adsorbed on the surface (Guzm, 2005; Rehman and Bonfield, 1997). A weak band of CO_3^{2-} was detected in the region around 1567.78 cm^{-1} . This band indicates or confirms the minor amount of carbonate substitution. The vibrations of the O-P-O bonds corresponding to the absorption band of PO_4^{3-} appeared at 580 cm^{-1} indicate the bending mode of PO_4^{3-} . The peak at 976.89 cm^{-1} corresponds to symmetric stretching mode of PO_4^{3-} . The most intensive band that appeared at 1060 cm^{-1} corresponds to the asymmetric stretching vibrations of the P-O (Lak et al., 2008).

The XRD analysis of the prepared HA shows the sharp narrow peaks indicated by 2θ from 25° to 32° . The crystalline peaks were observed at $2\theta = 25.8^\circ$, 31.8° , 39.8° , 46.7° , 49.5° and 51.5° , corresponding to HA. All the peaks of the prepared powders correspond to that of the standard HA that was reported in the ASTM card (JCPDS No. 74-0566); however, the peaks of the produced HA had different intensity than the standard one (Mohandes et al., 2014; Sobczak et al., 2009). These sharp narrow peaks are indicated that the prepared HA is a crystalline sample.

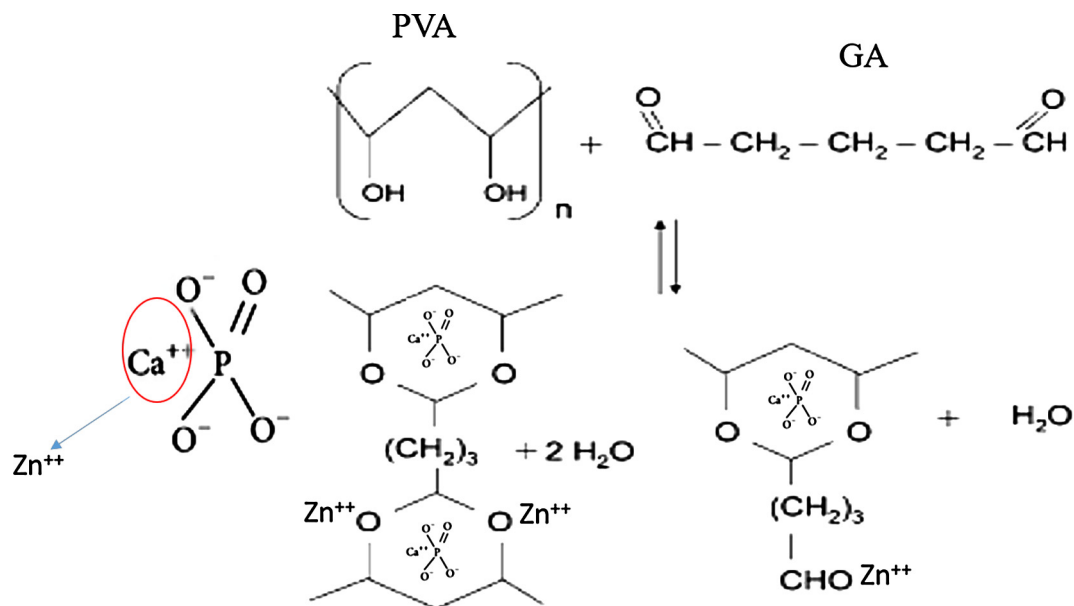


Figure 9 Mechanism of the reaction between GA and PVA during crosslinking process and shows the penetration of HA inside the crosslinked chains.

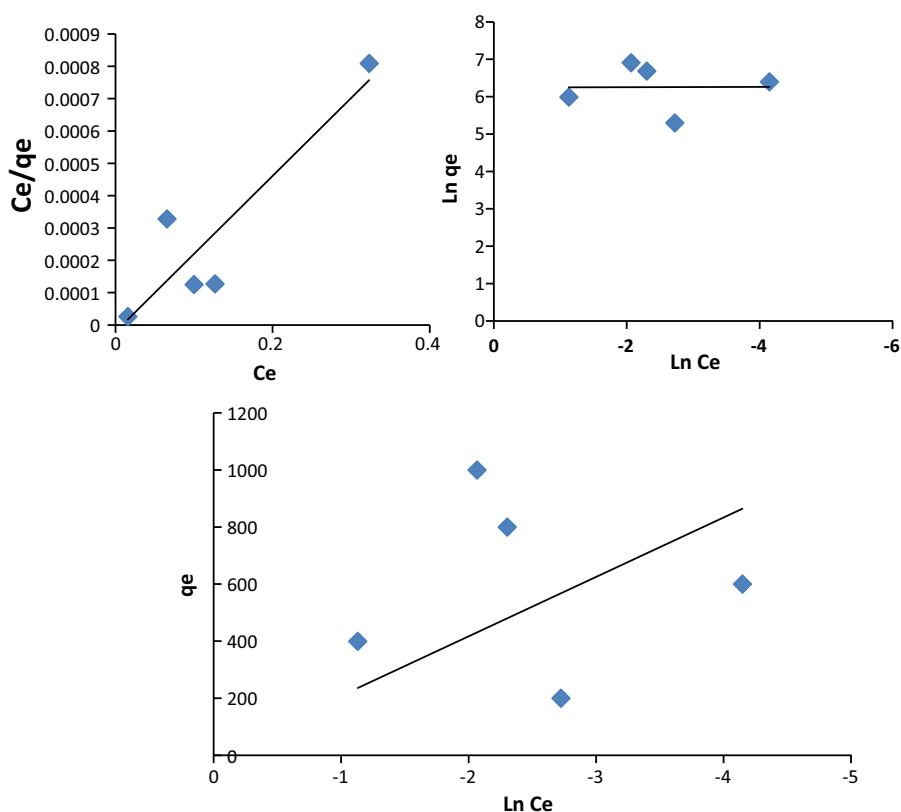


Figure 10 Langmuir, Freundlich and Temkin isotherms of Adsorption of Zn²⁺ by PVA nanofibers.

3.2. Characterization of polyvinyl alcohol (PVA) nanofibers

Fig. 3 shows the representative surface morphologies of electrospun PVA nanofiber membranes with different concentrations of PVA/H₂O solutions (5, 8, 10) wt%. Scanning

electron microscopic evaluation revealed the formation of solid, uniform, nanofibers with random orientation. The massive increase in an electrostatic repulsion that present in a high concentration tends to decrease the fiber diameters and induce an increase of the surface area (Adzila et al., 2013; Ting et al.,

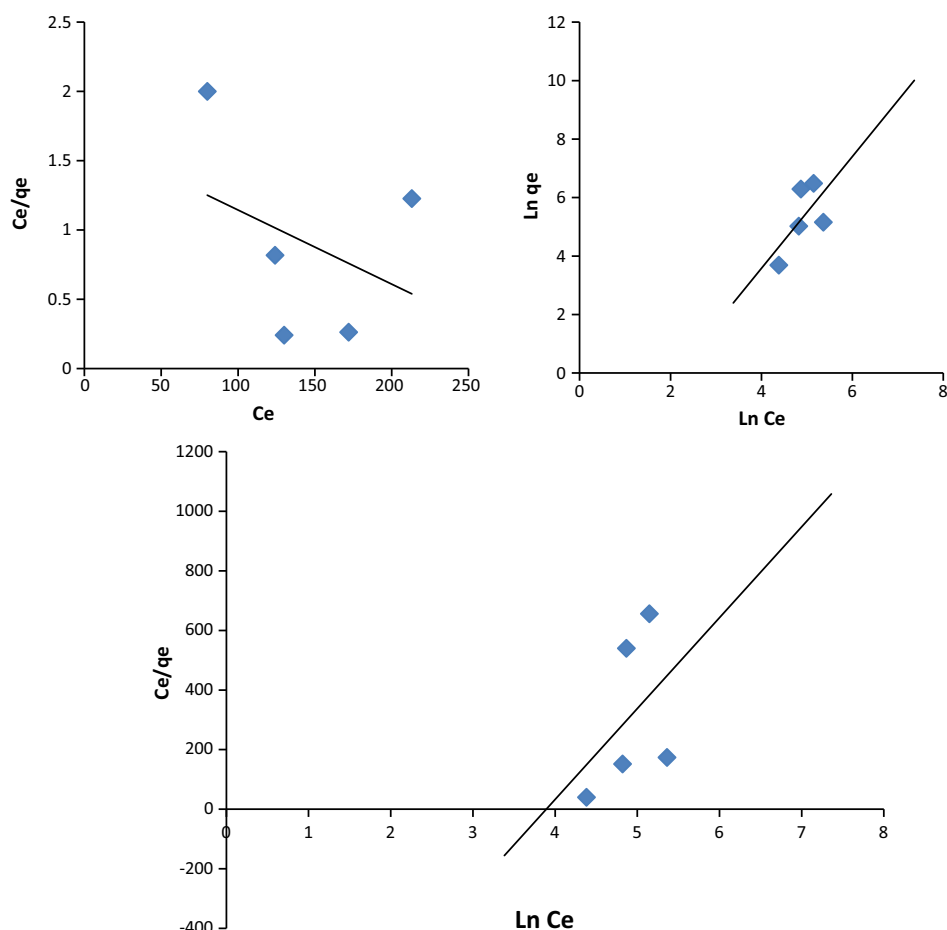


Figure 11 Langmuir, Freundlich and Temkin isotherms of Adsorption of Zn^{2+} by PVA/1% HA nanofibers.

2011; Rajzer et al., 2012). The 10% PVA nanofiber diameters are $(231.5 \pm 80 \text{ nm})$ which are the smallest fiber diameters if compared with (5, 8)% PVA solutions. For concentration (10% PVA/ H_2O solution) a series of experiments were carried out. The solution was pushed out from the syringe tip with constant flow rate of 0.5 mL/h and the applied voltage was varied between “15 and 30” kV with constant distance between tip and the collector 20 cm. The mean average diameter of the fibers was “15 and 30” kV as follows: $(231.5 \pm 80 \text{ nm})$ and $(172.5 \pm 45 \text{ nm})$ respectively.

3.3. Characterization of the cross-linked PVA nanofibers

Fig. 4A shows the mechanism of the crosslinking reaction of GA with PVA nanofibers. The strategy used to investigate the acid-free reaction between PVA and GA to form the A and B reversible structures (Zhang et al., 2013). The crosslinking ‘contracted’ nanofibers within the nanofiber mats, produce a denser structure with closely packed nanofiber membranes (Liao et al., 2010) that is shown in Fig. 4B.

3.4. Characterization of nanocomposite PVA/HA nanofibrous membrane

The encapsulation of nano-HA in PVA nanofibers was characterized by SEM that is shown in Fig. 5. The spherical HA

particles were mostly oriented along the axial direction inside individual fibers, whereas a few were perpendicular to axial direction extruding the fibers (Song et al., 2012). The elemental composition of nanofibers determined by EDX reveals the components (Ca, P) (3.69, 2.01) respectively that are encapsulated within fibers.

Table 1 Isotherm parameters for Adsorption of Zn^{2+} by PVA nanofibers and PVA/1% HA.

Isotherm	Parameters	
	PVA (NF)	PVA/1% HA
<i>Langmuir model</i>		
R^2	0.8149	0.1354
K_L	$-5 * 10^4$	0.595
a_L	-120	$-3.16 * 10^{-3}$
<i>Freundlich model</i>		
R^2	$3 * 10^{-5}$	0.795
K_f	$1.7 * 10^5$	$8.46 * 10^{-5}$
$1/n_f$	-0.0032	1.9125
n_f	-312.5	0.522
<i>Temkin model</i>		
R^2	0.646	0.1766
B	-208.37	304.98
A	1	0.020

The FT-IR analysis of the prepared membranes of PVA nanofibers and nanocomposite of PVA/HA nanofibrous membranes is shown in Fig. 6. The bands at 1316, 3348 cm^{-1} are associated with C—O—H stretching of PVA and O—H bonding in PVA. The band at 1150 cm^{-1} was (C—O—C) formed through the crosslinking between OH of a typical PVA structure and —C— of GA molecule. Furthermore, the strengthening of the band at 1720 cm^{-1} is indicative of C=O bond which is characteristic of GA (Shaikh et al., 2012). The band at 2850 cm^{-1} appeared on both PVA nanofibers and nanofiber composite, which revealed that (O=C—H) of the GA structure (Figueiredo et al., 2008; Shaikh et al., 2012).

3.5. Removal of Zn^{2+} from the wastewater

Figs. 7 and 8 show the removal percentage of Zn^{2+} from the simulated water by using nanofibrous (PVA, PVA/HA) membranes. Different concentrations of Zn^{2+} solutions (100, 200, 300, 400 and 500) ppm have been studied as a function in time until 2 h.

Fig. 7 shows the removal percent of Zn^{2+} by using PVA nanofibrous (50 mg) membranes with constant stirring rate 300 rpm. The adsorption amount increases sharply up to 15 min and then still constant (100% removal percent) until 2 h. However, the removal percent of Zn^{2+} by using (PVA/HA) nanofiber membranes with the same conditions is variable with different Zn^{2+} concentrations as shown in Fig. 8.

The adsorption amount increases sharply up to 20 min then it seems constant up to (15, 45, 50, 55)% removal percent and the large adsorption amount with 500 ppm simulated solution. The initial increase might be due to high surface area and inter or intra nanofibrous pores that present in nanofibrous membranes (Song et al., 2012). The removal % of Zn^{2+} in case of nanocomposite was less than PVA nanofibrous membrane. Unfortunately, the hydroxyapatite effect negatively on the adsorption capacity of the composite may be due to the penetration of the particles of HA inside the chains of PVA cross-linked polymeric structure (Roland, 2014), so decrease the surface area of the nanocomposite and also blocking of the active groups composite that has been shown in the following Fig. 9.

3.6. Studying the adsorption isotherms

Fig. 10 shows the kinetic isotherms of Langmuir, Freundlich and Temkin respectively for adsorption of Zn^{2+} by (PVA) nanofiber membrane, while Fig. 11 shows the same kinetic isotherms for adsorption of Zn^{2+} by (PVA/1% HA) nanofiber membrane. Table 1 summarizes the results of the isotherm constants for the three different equilibrium isotherms tested.

On the basis of the correlation coefficients (R^2), for the Langmuir model ($R^2 = 0.8149$), it was evident experimental data fit for the linear Langmuir isotherm equation model for adsorption of Zn^{2+} by PVA nanofiber membranes, while the PVA/HA nanofibers, the data fitting for Freundlich and Temkin models $R^2 = (0.866, 0.751)$ respectively. The results show that the adsorption in case of PVA nanofibers takes place as a monolayer homogenous adsorption with the nanofibrous surface, but in case of addition of HA to PVA nanofibers the adsorption of Zn^{2+} takes place as a heterogeneous adsorption.

4. Conclusions

In this work, we successfully fabricated polymeric nanofibrous (PVA and PVA/HA) composites. The comparison study of the fiber diameters of the different concentrations (5, 8, 10) wt% indicated that the 10% PVA nanofiber diameters have the smallest fiber diameters (231.5 ± 80 nm) if compared with (5, 8) wt% PVA solutions. Potential applications based on such fibers specifically their use as adsorbent in wastewater treatment have been realized. After the crosslinking of the polymeric nanofibers (PVA and PVA/HA) with GA, they were used for removal of Zn^{2+} from a simulated water. The adsorption process was studied by the isotherm models such as Langmuir, Freundlich and Temkin. The Zn^{2+} adsorption process with PVA and PVA/HA nanofibrous membranes was fitted to Langmuir and Freundlich isotherm models respectively. Therefore, the prepared PVA/HA nanofiber composite would be a promising material that can be used in the removal of heavy metals.

References

- Abdous, M., Shoushtari, M., Haji, A., Moshref, B., 2012. Fabrication of chelating diethylenetriaminated pan micro and nano fibers for heavy metal removal. *Chem. Ind. Chem. Eng. Quart.* 18, 27–34. <http://dx.doi.org/10.2298/CICEQ110719043A>.
- Adzila, S., Sopyan, I., Singh, R., Pusparini, E., 2013. Notes Mechanochemical synthesis of sodium doped hydroxyapatite powder. *Indian J. Chem.* 52, 739–743.
- Badmus, M.A.O., Audu, T.O.K., Anyata, B.U., 2007. Removal of heavy metal from industrial wastewater using hydrogen peroxide. *Afr. J. Biotechnol.* 6, 238–242.
- Dawid, A., 2001. Adsorption – from theory to practice. *Adv. Colloid Interface Sci.* 93, 135–224.
- Feng, C., Khulbe, K.C., Matsuura, T., Tabe, S., Ismail, A.F., 2013. Preparation and characterization of electro-spun nanofiber membranes and their possible applications in water treatment. *Sep. Purif. Technol.* 102, 118–135. <http://dx.doi.org/10.1016/j.seppur.2012.09.037>.
- Figueiredo, K.C.S., Alves, T.L.M., Borges, C.P., 2008. Poly (vinyl alcohol) films crosslinked by glutaraldehyde under mild conditions. *J. Appl. Polym. Sci.* <http://dx.doi.org/10.1002/app.29263>.
- Fonseca, E., Fábila, S., Sander, H., 2006. Synthesis and characterization of poly (vinyl alcohol) hydrogels and hybrids for rMPB70 protein adsorption. *Mater Res* 9, 185–191.
- Freitas, O.M.M., Martins, R.J.E., Delerue-matos, C.M., Boaventura, R.A.R., 2008. Removal of Cd (II), Zn (II) and Pb (II) from aqueous solutions by brown marine macro algae: kinetic modelling. *J. Hazard. Mater.* 153, 493–501. <http://dx.doi.org/10.1016/j.jhazmat.2007.08.081>.
- Guzm, C., 2005. Stoichiometric hydroxyapatite obtained by precipitation and sol gel processes. *Rev. Mex. Fis.* 51, 284–293.
- Haider, S., Park, S.Y., 2009. Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu(II) and Pb(II) ions from an aqueous solution. *J. Membr. Sci.* 328, 90–96. <http://dx.doi.org/10.1016/j.memsci.2008.11.046>.
- Illinois, S.O.F., (n.d.). State of Illinois.
- Kampalananonwat, P., Supaphol, P., 2010. Preparation and adsorption behavior of aminated electrospun polyacrylonitrile nanofiber mats for heavy metal ion removal. *ACS Appl. Mater. Interfaces* 2, 3619–3627. <http://dx.doi.org/10.1021/am1008024>.
- Lak, A., Mazloumi, M., Mohajerani, M.S., Zanganeh, S., Shayegh, M. R., Kajbafvala, A., et al., 2008. Rapid formation of mono-dispersed hydroxyapatite nanorods with narrow-size distribution via microwave irradiation. *J. Am. Ceram. Soc.* 91, 3580–3584. <http://dx.doi.org/10.1111/j.1551-2916.2008.02690.x>.
- Lan, T., Shao, Z., Wang, J., Gu, M., 2015. Fabrication of hydroxyapatite nanoparticles decorated cellulose triacetate nanofibers for

- protein adsorption by coaxial electrospinning. *Chem. Eng. J.* 260, 818–825. <http://dx.doi.org/10.1016/j.cej.2014.09.004>.
- Liao, S., Chan, C.K., Ramakrishna, S., 2010. Electrospun nanofibers: work for medicine? *Front. Mater. Sci. China* 4, 29–33. <http://dx.doi.org/10.1007/s11706-010-0009-0>.
- Mobasherpour, I., Salahi, E., Pazouki, M., 2011. Removal of nickel (II) from aqueous solutions by using nano-crystalline calcium hydroxyapatite. *J. Saudi Chem. Soc.* 15, 105–112. <http://dx.doi.org/10.1016/j.jscs.2010.06.003>.
- Mohandes, F., Salavati-Niasari, M., Fathi, M., Fereshteh, Z., 2014. Hydroxyapatite nanocrystals: simple preparation, characterization and formation mechanism. *Mater. Sci. Eng., C* 45, 29–36. <http://dx.doi.org/10.1016/j.msec.2014.08.058>.
- Rajzer, I., Kwiatkowski, R., Piekarczyk, W., Biniaś, W., Janicki, J., 2012. Carbon nanofibers produced from modified electrospun PAN/hydroxyapatite precursors as scaffolds for bone tissue engineering. *Mater. Sci. Eng., C* 32, 2562–2569. <http://dx.doi.org/10.1016/j.msec.2012.07.041>.
- Rehman, I., Bonfield, W., 1997. Characterization of hydroxyapatite and carbonated apatite by photo acoustic FTIR spectroscopy. *J. Mater. Sci. – Mater. Med.* 8, 1–4 <<http://www.ncbi.nlm.nih.gov/pubmed/15348834>> .
- Roland, C.M., 2014. Encyclopedia of polymeric nanomaterials. *Encycl. Polym. Nanomater.*, 1–9 <http://dx.doi.org/10.1007/978-3-642-36199-9>.
- Scalera, F., Gervaso, F., Sanosh, K.P., Sannino, A., Licciulli, A., 2013. Influence of the calcination temperature on morphological and mechanical properties of highly porous hydroxyapatite scaffolds. *Ceram. Int.* 39, 4839–4846. <http://dx.doi.org/10.1016/j.ceramint.2012.11.076>.
- Shaikh, R.P., Kumar, P., Choonara, Y.E., Toit, L.C., Pillay, V., 2012. Crosslinked electrospun PVA nanofibrous membranes: elucidation of their physicochemical, physicomechanical and molecular disposition. *Biofabrication* 4. <http://dx.doi.org/10.1088/1758-5082/4/2/025002>.
- Sharma, D.K., Li, F., 2014. Electrospinning of Nafion and Polyvinyl alcohol into nanofiber membranes: a facile approach to fabricate functional adsorbent for heavy metals. *Colloid Surf.: A Physicochem. Eng. Aspects.* <http://dx.doi.org/10.1016/j.colsurfa.2014.05.038>.
- Sobczak, A., Kowalski, Z., Wzorek, Z., 2009. Preparation of hydroxyapatite from animal bones. *Acta Bioeng. Biomech./Wrocław Univ. Technol.* 11, 23–28 <<http://www.ncbi.nlm.nih.gov/pubmed/20405812>> .
- Song, W., Markel, D.C., Wang, S., Shi, T., Mao, G., Ren, W., 2012. Electrospun polyvinyl alcohol-collagen-hydroxyapatite nanofibers: a biomimetic extracellular matrix for osteoblastic cells. *Nanotechnology* 23, 115101. <http://dx.doi.org/10.1088/0957-4484/23/11/115101>.
- Ting, H.-N., Abu Osman, Noor Azuan, Abas, Wan Abu Bakar Wan, Wahab, Ahmad Khairi Abdul, 2011. In: *5th Kuala Lumpur International Conference on Biomedical Engineering*. Springer Shop.
- Wang, Y., Hsieh, Y., 2010. Crosslinking of Polyvinyl Alcohol (PVA) fibrous membranes with glutaraldehyde and PEG diacylchloride. *J. Appl. Polym. Sci.* <http://dx.doi.org/10.1002/app.31750>.
- Zhang, L., Aboagye, A., Kelkar, A., Lai, C., Fong, H., 2013. A review: carbon nanofibers from electrospun polyacrylonitrile and their applications. *J. Mater. Sci.* 49, 463–480. <http://dx.doi.org/10.1007/s10853-013-7705-y>.