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Grace Mary^a; Navin Chand^b; S. K. Bajpai^a

^a Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College, Jabalpur, M.P., India ^b Director Grade Scientist and Head, Polymer Composite Group Advanced Materials and Process Research Institute (Formerly RRL Bhopal), (CSIR), Bhopal, M.P., India

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A Novel Approach to Prepare Zn(II)-loaded Cotton Fibers with Antibacterial Property

GRACE MARY¹, NAVIN CHAND² and S. K. BAJPAI¹

¹Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College, Jabalpur (M.P.) 482001, India ²Director Grade Scientist and Head, Polymer Composite Group Advanced Materials and Process Research Institute (Formerly RRL Bhopal), (CSIR), Bhopal (M.P.) India

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This study is focused on investigating the feasibility of using poly(acrylamide-co-N-vinyl-2-pyrrolidone)-grafted cotton fibers for the release of Zn(II) ions under physiological conditions.

The optimum grafting conditions for ceric ammonium nitrate induced graft-copolymerization of acrylamide and N-vinyl-2pyrrolidone onto cotton fibers was found to include initiator concentration of 35 mM, catalyst HNO₃concentration of 0.35 M and initiation time of 10 min. The Zn(II)-loaded grafted fibers released Zn(II) in the physiological fluid for nearly 72 h with first order diffusion constant 6.0×10^{-4} min⁻¹. The release was regulated by ion-exchange mechanism and less release was observed in protein solution. The Zn (II) — loaded fibers exhibit fair antibacterial activity.

Keywords: Grafting, cotton, zinc ions, activation energy, wound dressings

1. Introduction

Burn injuries are accompanied by major metabolic, endocrine and immune changes. Major burns are associated with reduced bone formation and re-sorption in both adults and children (1). Metal ions such as Zn, Cu play an important role in collagen crosslinking and therefore, aid in the normal formation of bone matrix (2). Zinc stimulates bone formation and mineralization, and reduces bone resorption. It has also been reported recently that zinc plays an important role in skin health and function, with zinc deficiency causing moderate to severe dermatitis. Zinc-based enzymes and protein that direct the process of skin generation is especially evident during wound healing and inflammation reduction (3). Zinc deficiency can lead to delayed closure of wounds and ulcers. It also affects the immune system by causing a reduction in lymphocytes, which leads to an increased susceptibility to recurring infection and poor wound healing. High needs for zinc can be supplemented externally through topical zinc delivery, for example, by the use of zinc-paste bandage (4, 5). Therefore, it is clear that for burn wounds, where the loss of zinc ions is common, delivery of zinc through the use of appropriate zinccontaining dressing may be useful.

Fibers, made from natural sources, especially polysaccharides have been considered as the most promising dressing material due to their excellent biocompatibility, nontoxicity and potential bioactivity at the wound surface. These include alginates (6), chitin and chitosan (7, 8), cellulose (9), etc. Most recently, Qin et al. (10, 11) have reported chitosan fibers as wound dressing material for the release of potential ions like Zn++ ,Cu++ and Ag+ to produce antimicrobial effect and to enhance bone-formation and skin generation. However, products made from pure chitosan fibers have not been commercially viable due to high processing casts involved (deproteination, demineralization, and deacetylation processes are required to produce chitosan material of adequate purity) and availability of such purified material is still insufficient for large industrial scale fiber production. Poor textile processing properties of resulting fibers has also been a major problem.

Cellulose is a non-toxic, biocompatible and cheap polymer which is present at its appreciably higher concentration in cotton (12). The monomer N-vinyl-2-pyrrolidone (VP) is an excellent biocompatible material and used frequently in the manufacturing of contact lenses (13). Although, the other monomer, acrylamide (AAm) is a well known neurotoxin with good transdermal permeation, its safe use can be ensured by complete removal of unreacted monomer from the grafted product. As for as skin permeation of

Address correspodence to S. K. Bajpai, Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College, Jabalpur (M.P.) 482001, India. E-mail: mnlbpi@rediffmail.com; sunil.mnlbpi@gmail.com

polyacrylamide is concerned, it cannot permeate through skin due to its high molecular weight. It has also been used as a filling material by surgeons for treatment of depressions and wrinkle of the glabella, malar and upper lip region, lip augmentation nammaplasty, phalloplasty, atrophy or paralysis of the vocal cords (14).

To overcome the problems related with the use of chitosan fibers, we hereby propose cellulose based fibers (e.g. cotton fibers) as an alternative material to be developed and used in wound dressing for release of potential zinc ions. Since cellulose does not contain strong metal-ion binding groups like amine functionality in chitosan, first we have graft-copolymerized acrylamide (AAm) and N-vinyl-2-pyrrolidone (VP) on to cotton fibers so that zinc ions can be easily loaded into graft co-polymer networks attached along the cellulose chains in cotton fibers.

2. Experimental

2.1. Materials

The monomers acrylamide(AAm) and N-vinyl-2-pyrrolidone (VP), crosslinker N,N'-methylene bisacrylamide (MB) and initiator ceric ammonium nitrate (CAN) were obtained from Himedia, Mumbai, India. The catalyst nitric acid (HNO₃) and other chemicals were also analytical grade and received from S.D. Fine Chemicals, Mumbai, India. Cotton fibers were obtained as a gift from a local textiles mill.

2.2. Grafting procedure

All procedures, from solution preparation to the graft copolymerization, were performed at room temperature. Both the initiator (CAN) and monomer/crosslinker were dissolved in 0.36 M HNO₃, and bubbled with N₂ gas. Preweighed cotton fibers were put in 50 ml of 35 mM CAN solution for 10 min, washed with tap water to remove extra CAN, and then immersed in 25 ml of solution, containing pre-determined quantities of monomers AAm, VP and crosslinker MB. After graft polymerization reaction, the substrate was washed in acetone to remove homopolymer formed (16) and then equilibrated in distilled water for 48 h to remove unreacted salts. This step was essential in removing all unreacted monomers from the grafted product. Finally, the grafted fibers were dried at 40°C in a dustfree chamber till the fibers attained constant weight. The percent grafting (PG) was calculated using the expression (15):

% Grafting (PG) =
$$\frac{W_g - W_o}{W_g} \times 100$$

Where W_o and W_g are the sample weights before and after graft co-polymerization, respectively. In all the

experiments, the ratio of weight substrate (g) to volume of monomer solution (ml) was kept at 1:250.

2.3. Instrumentation characterization

The FTIR-spectra of plain and grafted fibers were recorded with a Shimadzu spectrometer (UV 1700) using KBr mixed disc/pallet. The morphological features of grafted fibers were observed by using a JOEL JSM 840A (JAPAN) scanning electron microscope. DSC analysis was performed with a Mettler DSC-30 thermal analyzer with plain and grafted fibers of known weight (ca. 2.4 mg) in sealed aluminum pans. The samples were heated from 40°C to 260°C at the heating rate of 20°C/min under the constant flow of Argon gas. These measurements were done at Regional Research Laboratory (RRL), Bhopal (M.P.) India.

2.4. Water uptake analysis

Completely dry pre-weighed grafted cotton fibers were put in 250 ml of phosphate buffer solution of pH 7.4 at 37° C and their mass was measured at different time-intervals till the attainment of a constant weight. The percent mass-swelling (%Ms) was calculated using the following equation (17):

$$\% Ms = \frac{Swollen weight - Dry weight}{dry weight} \times 100$$

All the experiments were carried out with five samples and average values have been reported in the data.

2.5. Loading of Zn (II) ions into the grafted fibers

Pre-weighed dry fibers were put in aqueous solutions of Zn (II) ions of definite concentration. The fibers were taken out after 24 h and their mass was measured using a sensitive electronic balance (Denever, TB-124). The percententrapment efficiency of fibers was calculated using the following empirical equation:

Percent Entrapment Efficiency (PEE) =
$$\frac{W_L - W_O}{W_O} \times 100$$

Where W_o and W_L are the fiber weight before and after loading.

2.6. Zn^{++} ions release study

To investigate the release of Zn^{++} ions from the grafted cotton fibers (GCF), fiber samples of known weight were placed in contact with 40 times their own weight of a physiological fluid composed of 142 mM of sodium chloride and 2.5 mM of calcium chloride, thus representing the typical ion concentrations of body fluid as specified by the British Pharmacopeia (18). In order to investigate binding of Zn^{2+} ions with protein, a 3% soyabean solution was also used as a release medium. The amount of Zn^{++} ions, released at different time intervals, was measured volumetrically using EDTA method (19).

2.7. Microbial experimentation

For qualitative measurement of microbial activity, approximately 10^8 colony-forming units (CFU) of *E. Coli* were cultured on a Nutrient agar plate supplemented with Zinc(II)loaded fibers that were placed at the center of the plates. The plates were examined for a possible clear zone around the fibers after incubation at 37°C for 2 h. The plate, with plain fibers, was used as control set.

3. Results and discussion

3.1. Mechanism of grafting

A graft copolymer is a system comprised of a backbone material (cotton cellulose in this case) to which a second polymer is attached (poly(AAm-co-VP) in this study) at reactive sites along the macromolecular chains. The mechanism of graft copolymerization of vinyl monomers onto cellulose, as described by a number of workers (20, 21), may be briefly given as below.

In the presence of an acid used, HNO₃ (HA), primary radical species formation occurs as a result of the action of acid on Ce(IV):

$$Ce^{4+} + HA Ce^{3+} + H^{+} + A^{*}$$

Once the free radical species $(A^*) \rightarrow$ are formed, they produce cellulose macroradical via direct abstraction of hydrogen atom from cellulose molecules.

$$Cell-OH + A^* \rightarrow Cell-O^* + HA$$

Where Cell-OH represents cellulose molecule. Cellulose macroradical may also be formed by direct attack of Ce ⁴⁺ ions on cellulose molecule via H abstraction

$$Cell-OH + Ce^{4+} \rightarrow Cell - O^* + Ce^{3+} + H^+$$

When monomer molecules approach these cellulose macroradicals, graft-copolymerization reaction proceeds.

3.2. Selection of grafting procedure

In order to decide the method of graft copolymerization, we adopted the following three approaches.

In the first approach, pre-weighed cotton fibers were put in 50 ml of 35 mM CAN solution for 10 min (we call this the initiation step), then taken out and blotted with a filter paper to soak extra CAN solution, and finally put in 25 ml of aqueous solution containing pre-determined quantities of monomers/crosslinker. After the polymerization was over, the grafted fibers were put in acetone to remove homopolymer formed, and then equilibrated in water for 72 h, followed by drying in a dust-free chamber at 40°C. In the second approach, after the initiation step, the fibers were washed in running water for 1 min to remove extra CAN solution and then put in monomer solutions for polymerization to take place as mentioned in the previous paragraph. Finally, in the third approach, the fibers were not blotted with paper or washed with running water, after the initiation step. They were directly transferred into a reaction mixture for grafting reaction followed by washing in acetone, then equilibration in distilled water and finally drying at 40°C.

On the basis of the order of extent of grafting obtained in the above three approaches, i.e., second approach> first approach>third approach, we decided to follow the second approach throughout the investigations. The relatively lower percent grafting, observed in the first approach, may simply be attributed to the fact that after the initiation step when fibers were pressed between filter papers to remove extra CAN, some traces of CAN must have been retained within the ultrafine networks in the fibers. When these fibers are put in monomers solutions, the excess CAN diffuses out into the solution phase and induces both complexation with monomers, as well as homopolymerization (22). Similar reasons can also be assigned to the minimum grafting observed in the third approach. In this approach, the excess CAN was not removed by any means, which resulted in almost minimum grafting. Therefore, it may be concluded that removal of all excess CAN after the initiation step is essential to get a maximum graft vield.

3.3. Characterization of grafted fibers

The IR-spectral analysis is usually carried out to confirm the grafting on a substrate. Figure 1 shows a comparative depiction of the spectra of plain and grafted fibers. The IR spectra of 1(A) and (B) clearly shows a broad band at 3350-3550 cm⁻¹, which is due to bonded OH and symmetrical and asymmetrical stretching of C-H is found at 2890 cm⁻¹ and 2760 cm⁻¹, respectively. This spectra 1(B) shows a very sharp and intense absorption at 1750 cm^{-1} . which is due to >C = O group of N-vinyl-2-pyrrolidone. Also a peak corresponding to the carbonyl group of the amide moiety of the acrylamide unit is observed at 1510 cm⁻¹. The NH bending vibration bend appeared at 1610 cm⁻¹. Thus, it is clear that the spectra 1(B) is of grafted fiber. The scanning electron micrograph of grafted fibers, as shown in Figure 2, also supports formation of graft-copolymer onto the fibers. The grafted polymer can clearly be seen on the surface of the ultrafine fiber. Finally, the thermograms of plain and grafted fibers are shown in Figure 3. The glass transition temperature of plain and grafted fibers are found to be 70°C and 115°C, respectively. This indicates that grafting of monomer AAm and VP onto cellulose backbone of cotton fiber makes it thermally more stable.



Fig. 1. FTIR spectra of (A)plain and (B) grafted fibers.

3.4. Effect of initiation time on percent grafting

The effect of time of immersion of fibers in the CAN solution (i.e., initiation time) on percent grafting was studied by putting pre-weighed cotton fibers in 35 mM CAN solution for different time periods followed by their transfer into 25 ml of the reaction mixture, containing 2 M of AAm, 78 mM of MB and 1.5 M of N-vinyl-2-pyrrolidone, for a total period of 1 h at 30°C. The results, as depicted in Figure 4, clearly indicate that an initiation time of 10 min



Fig. 3. DSC thermogram of (A) plain and (B) grafted fibers.

appears to be sufficient for maximum grafting of nearly 124%. It is clear that immersion time of less than 10 min is not sufficient for complete formation of free radicals along the cellulose chains in the fibers, thus resulting in lower percent grafting. Moreover, when the fibers are put in CAN solution for relatively longer time (i.e., more than 10 min), there is slight decrease in the percent grafting which may most likely be due to the over saturation of fibers with CAN solution and so some traces of CAN might have been left in the pores even after washing with distilled water. This extra unremoved Ce(IV) may hinder the graft



Fig. 2. Scanning electron micrograph of the grafted fibers.



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Fig. 4. Effect of initiation time on percent grafting.



Fig. 5. Effect of CAN concentration on percent grafting.

copolymerization process by inducing complexation and homopolymerization as discussed earlier, thus finally causing a slight decrease in the percent grafting.

3.5. Effect of initiator concentration

In order to study the effect of CAN concentration on the percent grafting, pre-weighed dry cotton fibers were put in a CAN solution of different concentrations, in the range 5 mM to 45 M, for a period of 1 h at 30°C. The results, as depicted in Figure 5 clearly indicate that for 35 mM CAN concentration, maximum grafting is observed. This may be explained as follows:- when the CAN concentration is below 35 mM, it may not be sufficient for generation of a maximum number of free radicals along the cellulose chains, thus resulting in insufficient grafting. However, when the CAN concentration is increased beyond 35 mM, a continuous decrease in the percent grafting is observed. This may be attributed to the presence of some traces of unremoved CAN solution of higher concentration within the pores of cellulosic fiber network. The traces of unremoved Ce(IV) inhibit the graft copolymerization within the fibers through complexation with invading monomers. Beside, initiator Ce(IV) is also reported to participate in the termination of graft chains (23). Therefore, it is logical to establish the fact that when Ce(IV) concentration is sufficiently high, the free radicals speed up the termination step, thus causing a decrease in the graft yield. Therefore, it appears that a CAN concentration of 35 mM is sufficient for optimum grafting onto the fibers. Almost similar results have been reported by us in a previous study (24).

3.6. Effect of catalyst concentration

The effect of catalyst concentration on the percent graft yield is depicted in Figure 6. It is clear that percent grafting increases with the increase in HNO₃ concentration up to 0.36 M, and then it begins to decrease with a further increase in catalyst concentration. The plausible explanation of such behavior is that HNO₃, in the grafting medium, assists the grafting, both by causing inter and intra crystalline swelling of the substrate and by acting as a catalyst



Fig. 6. Effect of HNO₃ concentration on percent grafting.

in the hydrolysis of cellulose, leading to unfolding of the cellulose chains and improvement of the monomers accessibility. On the other hand, when the concentration of acid increases beyond 0.36 M, it may be enough to cause the degradation of backbone chains of cellulose, as well as of graft chains. In addition, the fall in the graft yield may also be attributed to the enhanced coagulation of colloidal homopolymer, which might have been formed due to the presence of a trace amount of unremoved Ce(IV) in the solution and in the fibers structure at lower pH. This may retard the diffusion of monomer molecules into a fiber phase (25). Therefore, the percent grafting is observed to decrease when catalyst concentration exceeds 0.36 M.

3.7. Effect of temperature

The effect of reaction temperature on percent grafting was also investigated. The graft yield showed positive temperature dependence in the temperature range $20-40^{\circ}$ C as represented in the time-conversion curve in Figure 7. It is clear that percent grafting increases with temperature, which may be due to the fact that an increase in temperature causes faster diffusion of monomer molecules towards active grafting sites present along the cellulose backbone. The reduced viscosity of the reaction medium also enhances the monomers mobility (26).



Fig. 7. Effect of reaction temperature on the percent grafting.



Fig. 8. Effect of temperature of initiator solution on the grafting yield.

The activation energy for the graft-copolymerization reaction was calculated from the Arrhenius plot of logarithm of the initial rate of grafting (Rg) vs. the reciprocal of the temperature as shown in the inset in Figure 5. The overall activation energy for the graft reaction was found to be $16.85 \text{ kJ mol}^{-1}$.

We also studied the effect of variation in temperature of initiator solution i.e., CAN solution on the percent graft yield. For this, the cotton fibers were put in 35 mM aqueous CAN solutions at different temperatures, in the range 10-50°C, followed by their immersion in reaction system at 30°C for 1 h. The results, as depicted in Figure 8 clearly indicate that as the temperature of CAN solution is increased beyond 10°C, the percent grafting increases and attains maximum value at 30°C, which may be attributed to the increase in the rate of formation of free-radicals. However, when the temperature is further increased beyond 30° C, a slight decrease in the percent grafting is observed. This may be probably due to the fact that an increase in temperature may induce the recombination process, thus resulting in a decrease in number of grafting sites along the cellulose backbone. In addition, the possibility of slight breakdown of cellulose by HNO₃ at higher temperatures should also be taken into consideration.

3.8. Water uptake analysis of grafted fibers

Figure 9 depicts the percent mass swelling of grafted fibers as a function of time in the phosphate buffer solution of pH 7.4 at 37°C. It is very clear that grafted fibers show excellent water absorbency which may be attributed to the hydrophilic nature of both monomers, namely acrylamide and N-vinyl-2-pyrrolidone that have been grafted into cotton fibers. A close look at Figure 9 reveals that initially the rate of water absorption is quite high, while later on, grafted fibers absorb water at a moderate rate. The initial faster uptake of water may simply be attributed to the fact that when fibers come in contact with the swelling medium, the surface of the grafted fiber absorbs water rapidly. However,



Fig. 9. Water uptake of grafted fibers in the physiological fluid at 37° C.

when the water enters into the bulk of the grafted polymer network, its diffusion becomes relatively slower. The overall percent swelling, exhibited by grafted fibers was nearly 275% in 3 h.

3.9. Loading of Zn^{2+} ions into grafted cotton fibers (GCF)

The zinc ions were loaded into GCF by equilibrating a known quantity of completely dry grafted fibers in aqueous solutions of Zn(II) ions of definite concentrations. When fibers come in contact with aqueous medium, the grafted polymer network begins to absorb the solution. The zinc ions entrapped within the swollen polymer network may probably be complexed with oxygen atom in carbonyl group of vinyl-pyrrolidone unit through electronic attraction. To confirm this, we recorded FTIR spectrum of Zn(II)-loaded GCF and compared it with that of grafted fibers. It was observed that the peak, appearing at 1705 cm⁻¹ for CO group of N-vinyl-2-pyrrolidone in grafted GCF was shifted to 1633 cm⁻¹ in Zn(II)-loaded grafted GCF(as shown below).





Fig. 10. Percent entrapment efficiency of Zn(II) in grafted cotton fibers at different initial Zn(II) concentrations.

This indicates the binding of Zn(II) with oxygen of CO group of NVP in Zn(II)-loaded grafted fibers. Recently, silver ions have also been reported to form complex with N-vinyl-2-pyrrolidone (27).

We also determined percent entrapment efficiency (PEE) of Zn(II) ions. For this, pre-weighed grafted fibers were put in Zn(II) solutions of different concentrations, in the range 0.05 to 0.30 M, for a period of 24 h. Figure 10 is a bar-diagram, showing percent entrapment efficiency at different initial molar concentrations of Zn(II) solutions. It is clear that PEE decreases with the increase in the initial concentration of Zn(II) solutions. This is the most commonly observed phenomenon and may be attributed to the fact that an increase in initial Zn(II) concentration does not result in much enhancement in zinc ions loading into the grafted polymer due to a limited number of binding sites available for Zn^{2+} ions within the grafted network. The zinc ions-loaded samples shall now be designated as GCF(X) where the number X in paranthesis denotes the percent entrapment.

3.10. Release of Zn(II) from grafted fibers

While investigating the release of metal ions, it must be noted that body fluid has a complex composition and the various components have different binding abilities to zinc ions and therefore, the choice of contacting media is important. In a study of the composition of serum fluid formed after auxiliary dissection, Bonnema et al. (28) found that on the first postoperative day, the drainage fluid contained blood contents and a high concentration of creatine phosphokinase. After day 1, it changed to a peripheral lymphlike fluid that contained different cells and more proteins. Trengrove et al. (29) found that wound fluid, collected from leg ulcers, contained 0.6-5.9 mM/l glucose and 25-61g/l protein. Similarly, Fraohm et al. (30) analyzed the fluid from a postoperative wound, leg ulcers and a large blister. They found that wound fluid contained fragments of peptide. Looking to the variation in various wound fluid



Fig. 11. Dynamic release of Zn^{2+} ions from grafted cotton fiber (GCF) in physiological fluid (PF) at 37°C.

compositions, we decided to carry out our *in vitro* study in the physiological fluid (PF), as suggested by British Pharmacopoeia which contained 142 mM of NaCl and 2.5 mM of CaCl₂. The results of the release experiment, carried out with the zinc-loaded grafted fiber sample GCF in the physiological fluid (PF) at 37°C, are shown in Figure 11. It is clear that fibers released metal ions for a total period of nearly 72 h. The released data was applied on the 'First order' kinetic equation given as (31).

$$-\ln\left(1-\frac{Q_{t}}{Q_{o}}\right) = kt$$

Where Q_{\circ} is the initial amount of Zn(II) loaded into the grafted fibers and Q_t is the amount of metal ion released at time t; and k is the first order rate constant. The plot between $-\ln(1-Q_t/Q_{\circ})$ and t, as shown in the Figure 12, was fairly linear with a regression value of 0.996. Such a higher regression confirms that release of Zn(II) from fibers can be described by first order kinetic model, with first order diffusion coefficient value of 6.0×10^{-4} min⁻¹ at 37°C.

As stated in the above paragraph, the wound fluid has been reported to also contain protein. Therefore, Zn(II) release was also studied in the 3% (w/v) aqueous soyabean solution at 37° C. Figure 13 shows a comparative depiction of the two release profiles obtained with protein fluid and



Fig. 12. First order kinetic plot.



Fig. 13. Comparative depiction of Zn(II) release in PF and protein solution at 37°C.

physiological fluid (PF) at 37°C. It is clear that Zn(II) ions are released at a faster release in the fluid PF. This indicates that the driving force, responsible for metal ion release, may not be actively operative in the protein fluid. These results lead us to think that the release of Zn^{2+} could probably be due to the ion-exchange process. To confirm this, we studied the Zn(II) release in the distilled water and compared it with the release data obtained in fluid PF. The results, as depicted in Figure 14 clearly indicate that nearly 20% Zn(II) ions are released in a duration of 72 h in distilled water. This finding supports our argument that the cations percent in the external solution (i.e., release medium) are responsible for the release of Zinc(II) from the fibers.

Therefore it may be concluded that when Zn(II)-loaded grafted fibers are placed in the release medium PF, which contains both sodium and calcium ions, the ion-exchange process takes place between the Zn^{2+} ions present in the grafted polymer network and cations in the release medium. However, the absence of exchangable cations in the distilled water causes almost negligible release.

3.11. Antibacterial property of Zn (II)-loaded fibers

The results of antibacterial test, as shown in Figure 15, clearly reveal that formation of bacterial colonies, surrounding the Zn (II)–loaded fibers is almost negligible which is indicated by the appearance of zone of inhibition



Fig. 14. Comparative depiction of Zn(II) release in PF and distilled water at 37°C.



Fig. 15. Photograph showing bacterial growth in the plates, (A) containing plain fibers and, (B) containing Zn(II)-loaded fibers. A clear zone of inhibition appears around the Zn(II)-loaded fibers in the plate shown in (B).

around the fibers. On the other hand, the plate containing plane fibers show a dense population of bacterial colonies throughout. This clearly indicates that Zn (II)–loaded fibers exhibit strong antibacterial activity.

Conclusions

From the above study, it can be concluded that cotton fibers can be effectively grafted with monomers acrylamide and N-vinyl-2-pyrrolidone via Ce(IV) induced grafted copolymerization in aqueous medium at 30°C. The grafted fibers can be easily loaded with potential zinc ions, which can be conveniently released from the fibers in the physiological fluid. These Zn (II)-loaded fibers show fair antibacterial property and therefore, put their strong candidature as dressing material for wound healing. However, this was only a preliminary investigation. A detailed study of Zn (II) release under various other significant parameters and investigation of their antibacterial activity *in vivo* are presently under investigations. These results shall be published in the near future.

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