Journal of Applied Polymer Science

Natural and Synthetic Polymers for Water Treatment Against Dissolved Pharmaceuticals

Abd El-Shafey I. Ahmed,[1] Hamed Y. Moustafa,[1] Ahmed M. El-Masry,[1] Salah A. Hassan[2]

[1]Department of Chemistry, Faculty of Science, University of Zagaizg, Zagazig, Sharkia, Egypt

[2]Egyptian International Pharmaceuticals Industries Company (EIPICO), 10th of Ramadan, Sharkia, Egypt

Correspondence to: A. El-Shafey I. Ahmed (E-mail: aiaibrahiem@zu.edu.eg or abdelshafey77@yahoo.com)

ABSTRACT: Dissolved pharmaceuticals were removed by adsorption on some natural and synthetic polymers. Cellulose, chitosan, and sodium alginate were selected as examples of natural polymers while a synthetic copolymer of epichlorohydrin and urea was prepared for comparison. Water contaminated with some antibiotics was treated with these polymers using stirred flask and column methods. The particles size of the investigated materials was increased up to 2 mm diameter by converting them into beads. Combinations of polymers, natural or synthetic, were used together to improve their behavior. The synthetic polymer has shown better removal effect than that of natural ones. It has removed up to 75% of the drug in 6 h. Chitosan was the best natural polymers in removing dissolved drugs; up to 13% of the drug has been removed by it. The recycling properties of the polymers loaded with drugs were examined and up to 9% of the drug was successfully restored. In addition, fully loaded dry beads with drugs were grounded and recycled in an ointment as blends. Moreover, the swelling behavior of the beads in different mediums and under different conditions was examined. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40458.

KEYWORDS: applications; blends; copolymers; separation techniques; cellulose and other wood products

Received 30 October 2013; accepted 16 January 2014

DOI: 10.1002/app.40458

INTRODUCTION

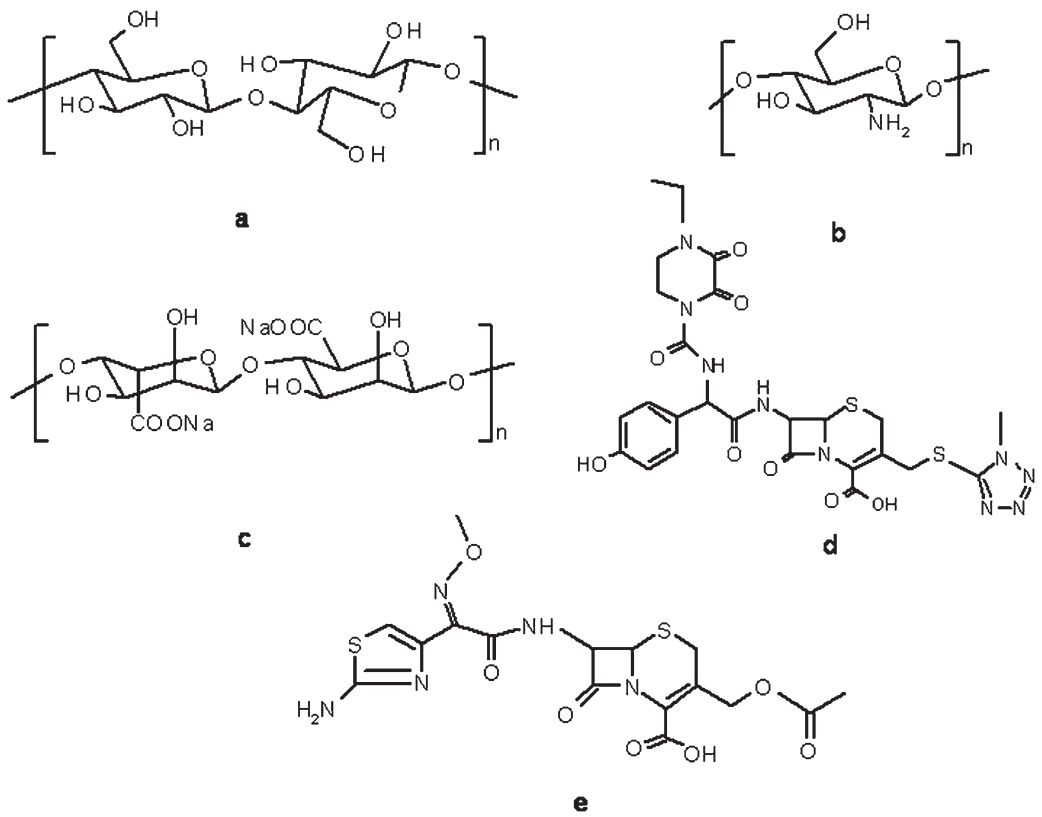
Pharmaceutical industry is producing a wide variety of products. It uses both inorganic and organic compounds as raw materials; the latter is either synthetic or natural.[1] This industry is producing a large amount of waste which is toxic to biological life.[2] During the last several decades, the production and consumption of pharmaceuticals are rapidly increased with the development of medical science; ~3000 compounds were used as medicine and the annual produced amount has exceeded hundreds of tons.[3–5] After their use, large amounts of pharmaceuticals are discarded into water system.[5] They have been detected in urban and livestock agricultural wastewater and surface water.[6–11] Furthermore, these pollutants may adversely impact aquatic ecosystem and human health by endocrine disruption and the development of antibiotic resistant bacteria (super bugs).[12–16] For these reasons, pharmaceutical contamination became an emerging concern in water resources worldwide.[17]

Burning biomass at some countries results in an air pollution problem with drastic effects to human health and economy.[18–22] This problem appears on a yearly base at some rice producing countries such as Egypt.[18–22] There are many suggested applications for these wastes such as paper, charcoal, clean water, cement, and animal food production[20–26] but the amount of waste is still very big. This enforces the farmers to burn it which resulting in a black cloud of smoke in the sky of such countries producing a serious pollution problem.

Polymeric adsorbents were known for their ability in removing water pollutants.[27] They have been studied to purify process streams and recover valuable species from diluted aqueous solutions.[22,28] Presence of certain function groups in the polymeric skeleton supports the treatment process and increases the chance of removing any contamination.[22,28]

Taking these facts into consideration and during our trails to find more applications to agricultural wastes, we are trying in this research work to remove pharmaceutical wastes from water using some natural and synthetic polymers. The results of this paper support the environmental protection by reducing both air (controlling biomass burning) and water pollution (removing dissolved drugs). Removing dissolved drugs will help in stopping the growth of super bugs.

The natural polymers used in this study were extracted from agricultural wastes such as cellulose [Scheme 1(a)], extracted from rice straw, or from some other forms of biomass such as



Scheme 1. Chemical structure of (a) cellulose, (b) chitosan, (c) sodium alginate, (d) cefoperazone and cefotaxime.

chitosan [Scheme 1(b)], extracted from shrimp,[29] and sodium alginate [Scheme 1(c)], extracted from brown algae.[30] These materials in addition to a novel prepared copolymer (Scheme 2) were evaluated for pharmaceutical waste removal in their main form or in beads like shapes using stirred flask and column methods. They were evaluated alone or as a combination of two of them as a form of blended beads. The concentration of pharmaceuticals in water was followed using HPLC before and after treating with polymers to measure the extent of removal. Recycling possibilities of removed drugs were examined in order to restore the removed drug. Moreover, the swelling behavior of the beads in water under different conditions was examined. This has included the determination of swelling properties in presence of different salts and at different pH values in addition to identifying their water retention at different temperatures.

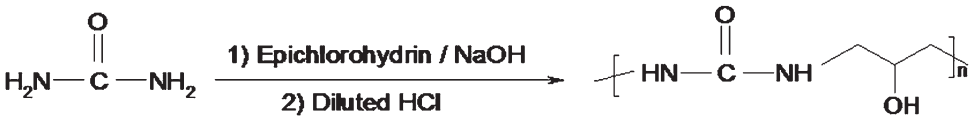
EXPERIMENTAL

Materials

Chitosan was supplied by Biochemika (Germany). It was extracted from crab shell (deacetylation degree 75–85%) with a molecular weight of 150.000. Alginic acid sodium salt was supplied by Acros Organics. Acetic acid (glacial, 100%) and epichlorohydrin were obtained from Merk, Germany. Calcium chloride and urea were obtained from El-Naser Company for Chemicals, Egypt. Sodium hydroxide pellets, cefoperazone sodium salt (purity 912.4μg/mg) as cefoperazone anhydrous [Scheme 1(d)], anhydrous cefotaxime sodium salt [purity 94.27%, Scheme 1(e)] and sulfuric acid were obtained from Fisher Scientific. All chemicals were used as supplied without extra purification. Cefoperazone or cefotaxime solutions were prepared by dissolving 0.1 g in 100 mL distilled water. The solution was first investigated by HPLC before dealing with fibers Figure 6(a). Rice straw was supplied by a local farm at east Nile Delta.

Analysis

Antibiotic concentration was detected using HPLC apparatus model Agilent 1200. The mobile phase was acetonitrile and phosphate buffer 0.05*M* with ratio 20 : 80 % (pH = 3.5). The column was BDS HYPERSIL C18 with dimensions 150 × 4.6 mm^2 and particle size of 5 μm. The flow rate was 1.5 mL/min while the wavelength of the used UV detector was 254 nm. The injection volume was 10 micro-litters. FTIR analysis was performed using IS 10 Nicolet FTIR (thermo scientific USA); IR SMART Omni-Transmission. The Scanning Electron Microscope (SEM)



Scheme 2. Preparation of urea epichlorohydrin copolymer.

Figure 1. Examples of prepared beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

photographs were carried out using SEM Model Philips XL 30 attached with EDX Unit, with accelerating voltage 30 KV, magnification 10–400.000×. The experiments were performed in replicates and the error bars in their corresponding figures have been removed as the error is too small to display.

Cellulose Extraction (Pulping and Bleaching)

Dry rice-straw (10 g) was grounded and soaked in sodium hydroxide solution (17.5%, 100 mL) in a 250 mL round bottom flask. The suspension was refluxed for 1 h and the resulting material was filtered, washed with distilled water till neutralization and dried at 100°C for 24 h. The cellulosic material was bleached using sodium hypochlorite (single stage bleaching).[31] Chemical analysis of raw materials has shown that the ratios of α-cellulose, hemicelluloses, and lignin were 37.2, 24.7, and 16.2%, respectively while after pulping they were 89.3, 8.6, and 0.8%, respectively. After bleaching the ratios of α-cellulose and hemicellulose were 90.3 and 0.6%, respectively, while the degree of polymerization was 762.6.[20,21]

Urea Epichlorohydrin Copolymerization, Synthetic Polymer (SP)

Urea, epichlorohydrin, and sodium hydroxide were heated in a round-bottom flask fitted with a reflux condenser in ratio of 1 : 1 : 1. After complete dissolving, a vigorous reaction was happened followed by the formation of a white precipitate. The refluxing continued until the entire liquid converted to white solid material. The prepared material was washed with water, diluted HCl, and methanol followed by drying in air over night (Scheme 2). The prepared polymer has shown the following analysis: FTIR υ (cm^{-1}): a broad band at 3400–3500 corresponding to NH and OH, a band at 2995 corresponding to CH aliphatic, a band at 1672 corresponding to C═O imide, and a

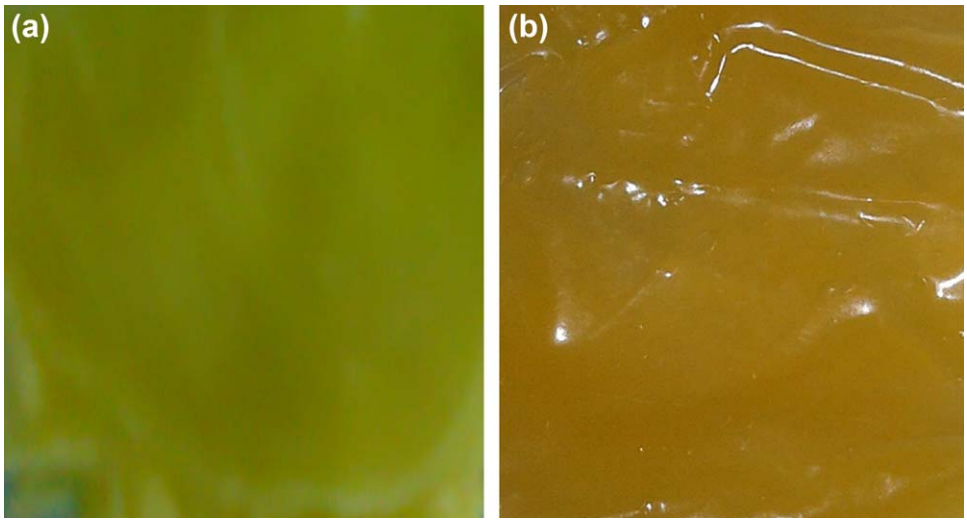


Figure 2. Ointment (a) before and (b) after blending with grinded Beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

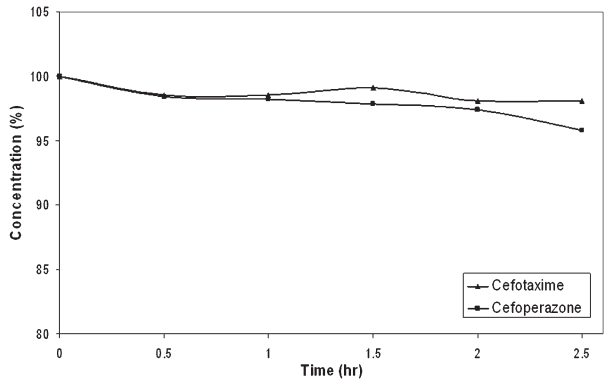


Figure 3. Assay of antibiotics after dealing with cellulose.

band at 1115 corresponding to C—O. Solid state ^{13}C-NMR (ppm): 40, 60, 70, and 160.

Preparation of Chitosan Beads (B1)

Chitosan (2 g) was dissolved in acetic acid (60 mL, 5% v/v). The viscous solution was added drop-wise to sodium hydroxide solution (500 mL, 0.5*M*). The acetic acid within the chitosan gel was neutralized and coagulated into spherical uniform beads. The aqueous sodium hydroxide solution was stirred continuously for 30 min. The chitosan beads were filtered, washed copiously with distilled water and dried using a piece of paper to remove the surface water.

Preparation of Alginate Beads (B2)

Sodium alginate (0.5 g) was dissolved in distilled water (10 mL). The solution was added gradually (drop-wise) to a solution of calcium chloride (5%, 50 mL) at ambient temperature. The mixture was stirred for further 1 h. The formed alginate beads were collected, washed copiously with distilled and dried using a piece of paper to remove the surface water.[32]

Preparation of Alginate Blended Beads (B3–5)

Alginate/chitosan beads (B3) was prepared using the following method: sodium alginate (1 g) was dissolved in distilled water (20 mL). Chitosan (0.15 g) was added gradually with stirring for 1 h. The resulting solution was added drop-wise to a solution of calcium chloride (5%, 50 mL) at ambient temperature under continuous stirring for 1 h. The formed beads were filtered and surface water was dried (Figure 1). Similar method was followed to prepare alginate/cellulose (B4) and alginate/synthetic polymer (B5) beads but using cellulose powder and synthetic polymer, respectively.

Preparation of Chitosan/Synthetic Polymer Beads (B6)

The chitosan solution was prepared by dissolving chitosan powder in acetic acid as described before. The viscous solution was left overnight followed by adding the synthetic polymer (0.15 g) gradually with stirring for 1 h. The formed mixture was added drop-wise into sodium hydroxide solution (500 mL, 0.5*M*). The formed beads were stirred for 30 min. Chitosan/synthetic polymer beads were filtered, washed with distilled water and dried.

Shaking Flask Method

This method was applied for the entire investigated materials in powder or bead like (dry or wet) shapes. In general the required material was shaken in the antibiotic solution for a certain period of time with sampling at timed intervals for HPLC analysis. The experiment was performed as follows: for powders; a preweighed amount of fibers (0.2 g) was challenged with the antibiotic (15 mL in a plastic bottle). The bottle was then shaken and sampled for HPLC at timed intervals; 0.5, 1, 2, 4, 6, 14, and 16 h. The same method was followed for wet and dry beads.

Column Method

Chitosan/synthetic polymer beads (wet beads, freshly prepared) were packed into 5 mL plastic syringe to form a column.[20,21,35] Cefoprazone solution (15 mL) was passed through the column. The perfused solution was recycled through the column for 10 runs by the action of gravity. Samples were collected before and after each run and the antibiotic concentration was followed using HPLC.

Recycling

Antibiotic Restoring. Chitosan beads (2 g) treated with cefoperazone resulting from the shaking flask method after the end of the experiment (16 h) was soaked in distilled water (14 mL). The shaking was started again for another 16 h with sampling at timed intervals; 0.75, 1.45, 2.45, 3.45, 4.45, 5.45, and 16 h for HPLC detection. The same experiment was performed for chitosan/synthetic polymer beads.

Antibiotic Redirection. The resulted beads after full saturation with the antibiotic were dried and grinded followed by blending with an ointment raw material as active ingredient to convert it

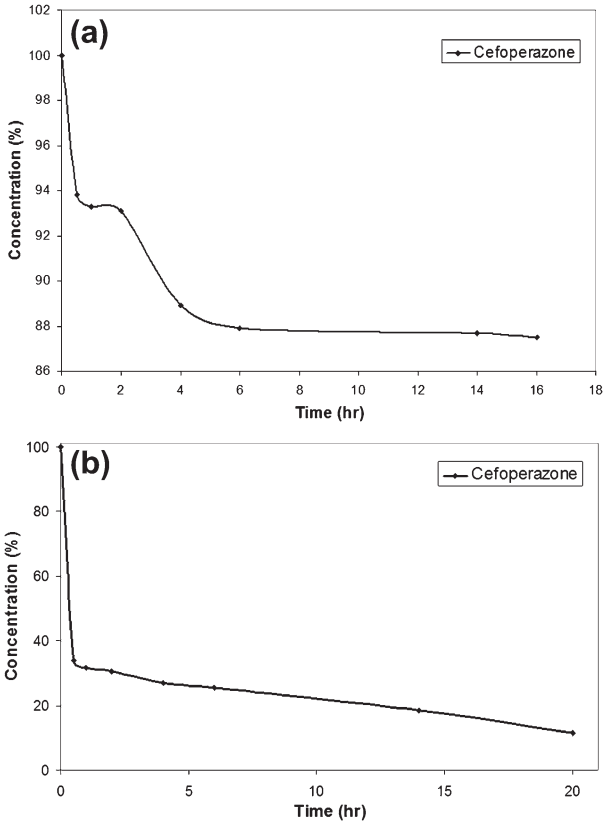


Figure 4. Assay of antibiotic after treating with (a) chitosan powder and (b) synthetic polymer (SP).

Table I. Assay of Dissolved Antibiotic After Treating with Different Beads

	Cefoperazone ratio (%) at timed intervals						
Type of bead	30 min	1 h	2 h	4 h	6 h	14 h	16 h
Chitosan beads (wet)	76.7	73.9	70.7	70.2	69.7	68.3	67.8
Alginate beads (wet)	89.5	89.9	89.7	88.9	87.0	84.9	85.0
Alginate/chitosan beads (wet)	92.8	93.9	93.7	90.9	89.9	88.5	87.0
Alginate/cellulose bead (wet)	91.2	91.2	91.5	90.9	89.9	89.7	86.0
Chitosan/synthetic polymer beads (wet)	77.2	75.3	73.7	70.9	69.7	66.3	63
Alginate/synthetic polymer beads (wet)	95.9	96.8	95	94.3	93.9	93.5	92
Chitosan beads (dry)	93.2	91.0	90.7	89.9	88.9	87.9	83.1
Alginate/chitosan beads (dry)	100	100	100	100	99.5	99.3	98.9
Alginate/synthetic polymer (dry)	100	100	100	99.9	99.8	99.7	99
Chitosan/synthetic polymer beads (dry)	100	95	93.9	92.4	91	89.8	84.9

to a local antibiotic for external use. The ointment raw materials were yellow soft paraffin, white soft paraffin, and lanoline (Figure 2).

Swelling Behavior of the Beads. The swelling behavior of prepared dry beads under different conditions was identified as follows: beads (chitosan or chitosan/synthetic polymer beads) (0.1 g) were soaked in tap water for 24 h. The beads were filtered, surface water was dried with a paper tissue and the swelling ratio was calculated using equation (1) at timed intervals. The same protocol was followed to determine the swelling behavior in distilled water and in saline solution (1% NaCl).[33] Moreover the swelling behavior was identified at different pH values. In addition the swelling behavior in presence of different salts with different valences such as $CaCl_2$ and $FeCl_3$ was identified in comparison with NaCl.[33,34] Water retention of beads have been identified by weighing a fully saturated beads with water (starting with 1 g) at different temperatures (25, 75, and 90°C) at timed intervals; 0.5, 1, 2, 4, 6, and 8 h.[33] This was performed for both chitosan and chitosan/synthetic polymer beads.

$$\text{Equation 1: Calculation of swelling ratio}$$
$$\%\ \text{Swelling} = (\text{Polymer weight after soaking} - \text{Polymer weight before soaking}) / \text{Polymer weight before soaking} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Escaping of pharmaceuticals to lakes and rivers supports the growth of high antibiotic resistance bacteria (super bugs). To help in stopping this phenomenon and to find more applications for the huge stock of biomass, different types of natural polymers were applied to remove such waste like cellulose extracted from rice straw, chitosan, and sodium alginate. In addition a synthetic polymer, prepared using urea and epichlorohydrin, was used to see the effect of some synthetic polymers in comparison with the natural ones. Moreover the effect of both synthetic and natural polymers in presence of each other as a form of blended beads was identified. The selection of these materials was based on the fact that they contain large number of hydroxyl or amino groups that are able to form hydrogen bonds with the function groups present in the antibiotic structure.

Starting with cellulose extracted from rice straw, the polymers were treated with different types of antibiotics (cefotaxime and cefoperazone) as examples for what can be found in waste (Figure 3). Presence of hydroxyl groups in cellulose structure may help in drugs adsorption by hydrogen bond formation. The results showed no significant loss of drug concentration with time up to 2.5 h. Chitosan was believed to have some effect due to the presence of amino groups in its structure which enables a better chance for hydrogen bonding. In literature it was reported that presence of certain function groups may enables the polymer to remove certain type of waste.[22,28] For this reason chitosan was used instead of cellulose in its insoluble powder status and the experiment was focused on one drug (cefoperazone) [Figure 4(a)]. It was noticed that better results have been obtained in the first 3 h more than that of cellulose which encourage extending the study up to 16 h. After this period of time it was noticed that up to 13% of the drug has been removed by the polymer [Figure 4(a)]. Maximum removal was reported at the first 6 h while later the absorption level became constant.

The results of chitosan has encouraged preparing some new synthetic polymer (SP) contains amide or amino groups which can

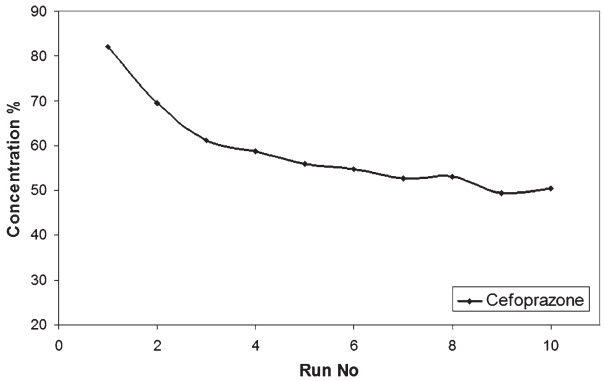


Figure 5. Cefoprazone assay in 10 cycles of column test.

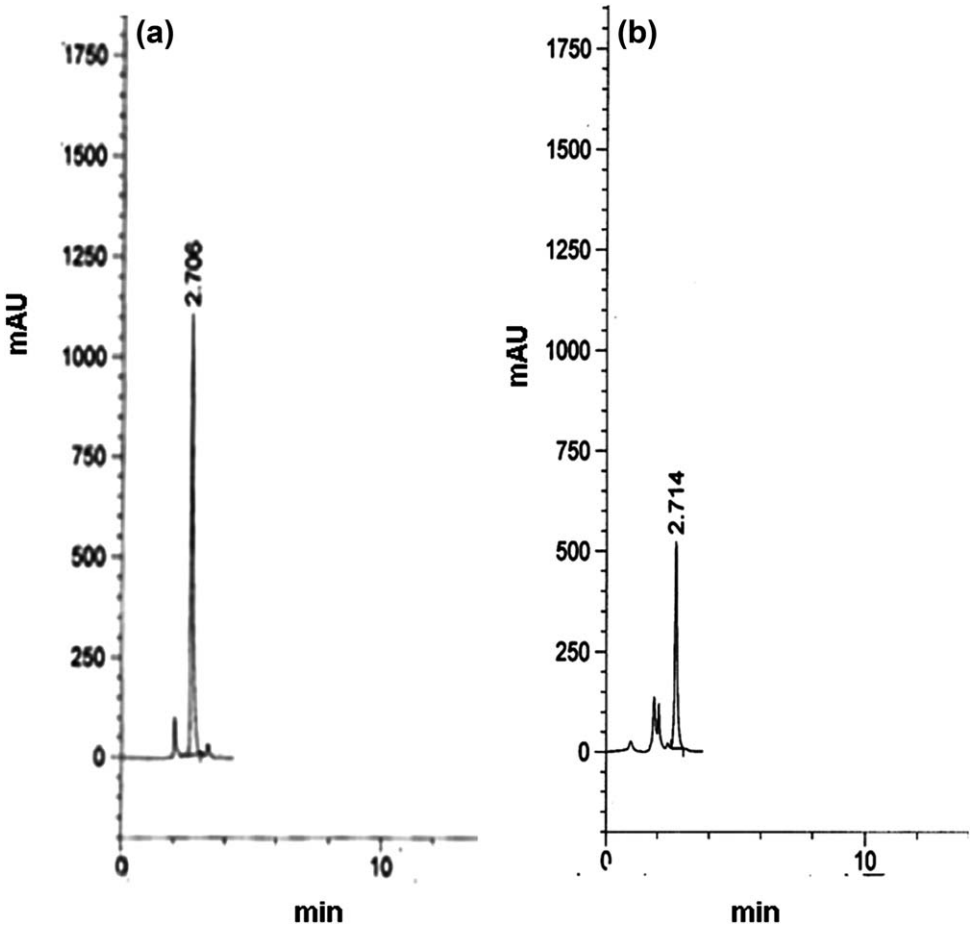


Figure 6. An example of HPLC analysis (a) cefoperazone standard and (b) cefoperazone after run 9 of chitosan/synthetic polymer beads column.

do similar job like chitosan and evaluated in this field for the first time in this study. For this purpose a low cost copolymer has been prepared by copolymerizing urea and epichlorhydrin in basic medium. The resulting polymer contains amide function groups in addition to hydroxyl ones, Scheme 2. The synthetic polymer was challenged with the drug in a similar protocol like chitosan [Figure 4(b)]. The results have indicated that a fast decrease in the drug concentration at the first 30 min was recorded and followed by a stable removal rate for the next time intervals. The effect of synthetic polymer in drug removal has exceeded chitosan. It has removed up to 75% of the drug in only 6 h of contact time with drug solution. This can be explained on the base that two nitrogen atoms are present in the synthetic polymer rather than one amino group in chitosan. The possibility of hydrogen bond as well as salt formation is increased in case of synthetic polymer.

Conversion of materials to a form of beads can increase the ratio of drug uptake and will not restrict the flow of water in case of their use in columns for water purification. The beads are providing more channels to accommodate high concentration of the drug. For this reason chitosan has been converted into beads and the same protocol was repeated to investigate the ability of the beads to remove drugs. Chitosan was dissolved into acetic acid followed by dropping into sodium hydroxide to form the required beads. Chitosan beads were treated with the drug directly after its preparation without drying (wet) or after complete dryness (dry) (Table I). Applying beads in its wet status enables the reaction with the polymer and the drug only without further absorption to water contains drug.

In addition, sodium alginate is a water soluble cellulosic material contains carboxylic function groups beside the hydroxyl ones so it was worse a try to compare its effect with chitosan and the synthetic polymer. Moreover, it can form beads in easy way by dropping into calcium chloride and other salts. Alginate beads can interact with the drug by hydrogen bonds formation through the carboxylate groups or it can carry some other polymers inside it as a form of blends[32,35] to increase their drugs uptake. Blending chitosan or alginate with other polymers such as cellulose or synthetic polymer may increase their uptake. For this reason chitosan and alginate have been blended with other types of fibers aiming to increase their action in removing the drug. The blended beads were investigated as wet and dry forms in some cases (Table I). Moreover chitosan was blended with alginate in mixed beads to see their behavior together.

Looking into Table I, chitosan has recorded good results alone in comparison with alginate beads. Using alginate did not improve the removal behavior even in presence of chitosan or

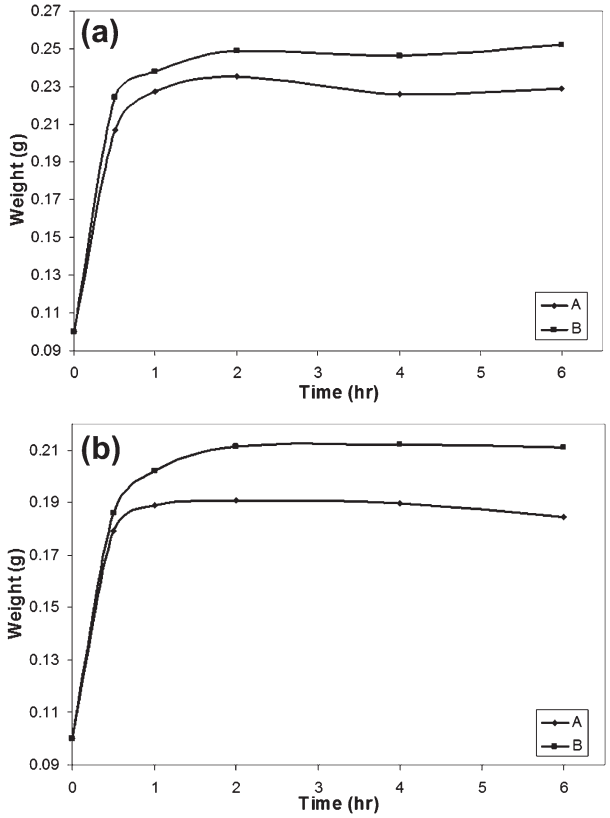


Figure 7. Water swelling for (a) chitosan beads and (b) chitosan synthetic polymer beads at A = tap water and B = distilled water.

synthetic polymer as blends. Blending cellulose with alginate has not improved its results. Blending the synthetic polymer with chitosan showed the best results while introducing the synthetic polymer with alginate has not improve the solo effect of alginate. It was noticed as well that wet beads have recorded better results than dry ones. This could be explained on the base that beads will take time to swell and absorb water while wet beads are already in its full saturated size which supports its ability to exchange the drug with solution.

The previous results indicated that natural polymers with alternative function groups are able to remove drugs from water. Amino groups showed better behavior than hydroxyl and carboxylate groups. The high results in case of amino group containing fibers may be due to the formation of hydrogen bonds due to the lone pair of electron on the nitrogen atom. The nitrogen atom as a hetero atom with low electronegativity makes its lone pair more available for hydrogen bond formation. In addition the presence of carboxylate group in the drug enables a formation of an ionic bond, ammonium salt formation. This behavior has increased in case of synthetic polymer due to the presence of two nitrogen atoms. It was clear that polymers in powder status have shown better results than beads due to the increase in the surface area. The best results between beads were recorded using beads formed from a blend between chitosan and synthetic polymer beads. For this reason their behavior was tested using another method; column method. Chitosan/synthetic polymer beads were packed in a column and a solution of cefoprazone was passed through it. The perfused solution was returned again to the column for recycling up to 10 cycles (Figure 5) with identifying the drug concentration after each cycle using HPLC (an example in Figure 6). It can be seen from Figure 5 that the column has succeeded in removing more than 40% or drug concentration which is encouraging the application of such materials in slow filtration techniques[36] in water treatment systems.

As the wet beads have recorded better results than dry ones so it was important to determine the swelling behavior of the prepared beads in different mediums and at different conditions. This behavior was evaluated in distilled, tap, and saline water. In addition, the swelling at different aqueous solutions contain ions with different valences was identified. The swelling behavior was studied as well at different pH values. Moreover their water retention at different temperatures was investigated by heating three different samples from the fully saturated beads at different temperature (25, 60, and 100°C).

Dry chitosan and chitosan synthetic polymer beads were soaked in distilled water and in tap water. The weight of beads was determined at timed intervals (Figure 7). It was noticed that water absorbance in distilled water is more than that in tap water or saline solution (Figures 7 and 8). Presence of high salt content around the beads decreases their ability to swell. Similarly, the swelling behavior at aqueous solutions contains ions in different valences such as NaCl, $CaCl_2$ and $FeCl_3$ with

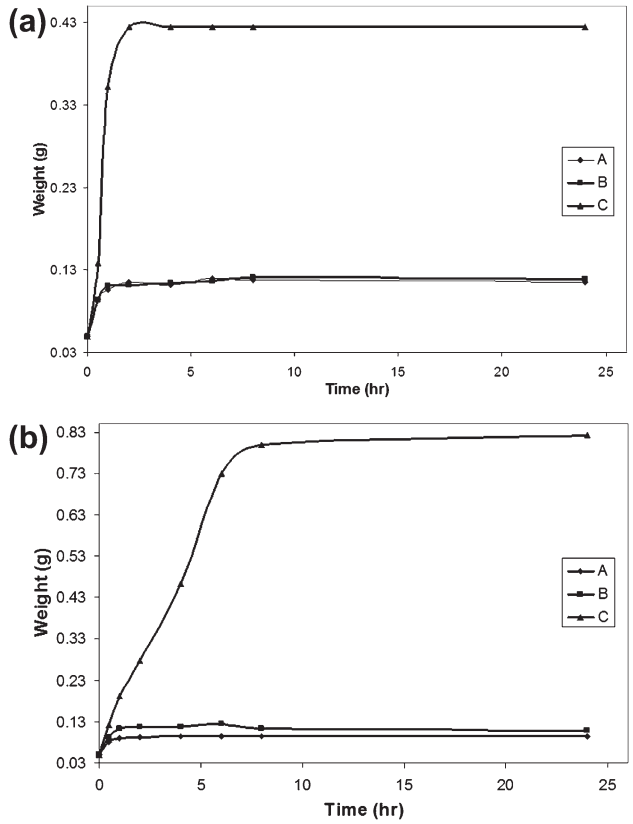


Figure 8. Water swelling for (a) chitosan beads and (b) chitosan synthetic polymer beads at A = NaCl, B = $CaCl_2$, and C = $FeCl_3$.

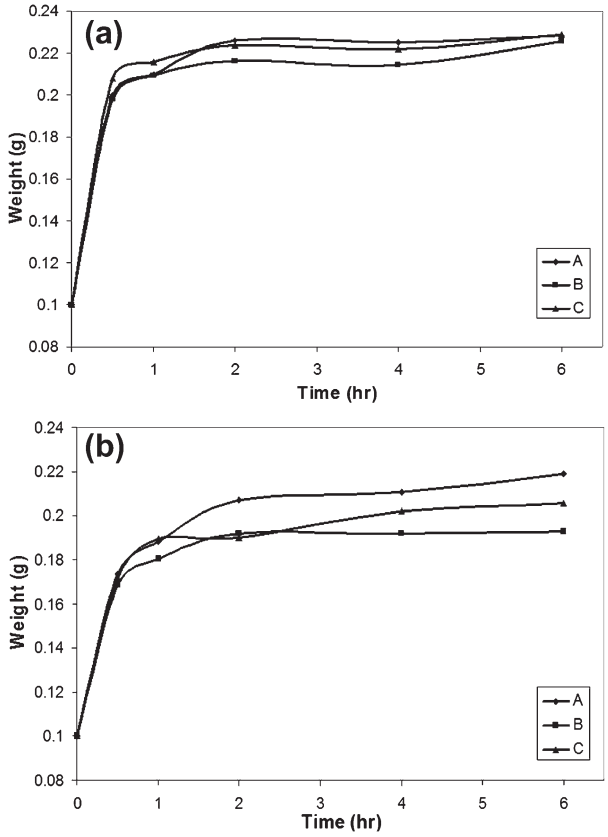


Figure 9. Water swelling for (a) chitosan beads and (b) chitosan synthetic polymer beads at different pH values A = 4, B = 7, and C = 9.

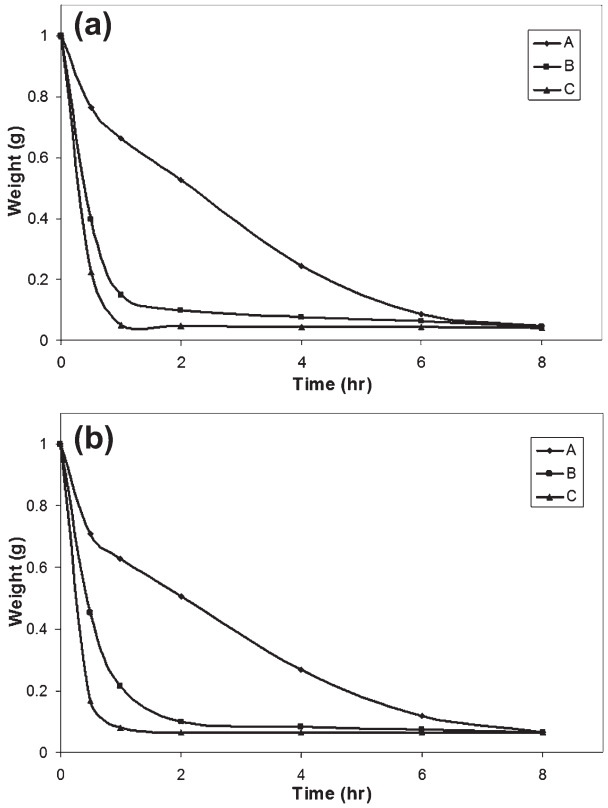


Figure 10. Water retention for (a) chitosan beads and (b) chitosan synthetic polymer beads at different temperatures (A = 25, B = 60, and C = 100°C).

concentrations up to 1% was determined (Figure 8). It can be seen form Figure 8 that swelling in presence of trivalent ions is more than that of di or monovalent ions. The swelling behavior in trivalent solutions was very fast and resulting in destroying the bead at certain stage (Figure 8). The pH of the medium was changed to investigate its effect on water absorbance. Dry beads were soaked in solutions with different pH values. It was noticed that the highest level of absorbance was recorded in acidic medium for both types of beads chitosan and chitosan synthetic polymer (Figure 9). It was noticed that increasing temperature has increased the loss of water with time for both types of beads. Increasing the temperature enables fast drying (Figure 10).

Recycling

Beads recycling are very important in order to restore the drug for economical goals. Restoring cefoperazone from beads (both chitosan and chitosan/synthetic polymer) was performed by soaking the fully saturated beads with drug into distilled water to release the drug. The concentration of released drug into water was followed using HPLC (Figure 11). The results showed that beads were able to release up to 7.5–8% of drug in just 45 min while it started to be stable around 9% for the next 16 h. Both types of beads, chitosan and chitosan/synthetic polymer, has recorded close results to each other (Figure 11). This has enabled thinking about another application for saturated beads with drugs which is grinding them after full dryness and blending with some kinds of ointment base materials (Figure 2). The drug was released with time form the ointment to the patient skin. This will be a base for another study for the clinical trials for such supported ointment (data will be published in due courses).

HPLC was the main tool of analysis in this study as it was able to detect the drug to the lowest possible concentration. Some other tools of analysis were tried to investigate the possible interaction with the fibers. FTIR, XRD, and SEM were performed to the beads before and after dealing with the drug. No differences or indication of presence of drug were recorded

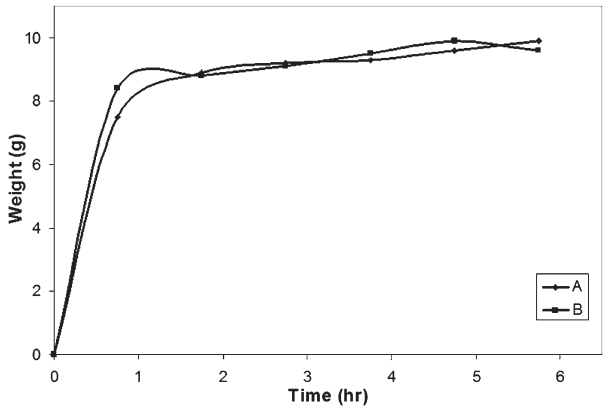


Figure 11. Cefoperazone released from different types of beads (a) chitosan beads and (b) chitosan synthetic polymer beads.

using FTIR and XRD. This could be explained on the base that the drug concentration is lower that the detection level using these tools in comparison with the main constituents of the materials, an example of XRD is shown in Figure 12. Looking into SEM photos (Figure 13) one can see the particles of the synthetic polymer blended with chitosan in case of chitosan synthetic polymer beads. Also comparing the dry beads with and without drug we can see a difference in a selected region called D. this region in dry beads with drug contain no lanes which we think that these lanes is filled with the drug so it disappeared by drying giving a smooth region in case of dry beads filled with drugs. But the most trustable way of analysis to follow the drug concentration was HPLC. The other methods have failed to record significant changes in the main expected beaks of the fibers or to give peaks related to the drug.

The previous results have indicated that pharmaceutical wastes can be removed by adsorption to natural and synthetic polymers at ambient temperature. This encourages further efforts on industrial level which will give economical value to this work in addition to its environmental importance.

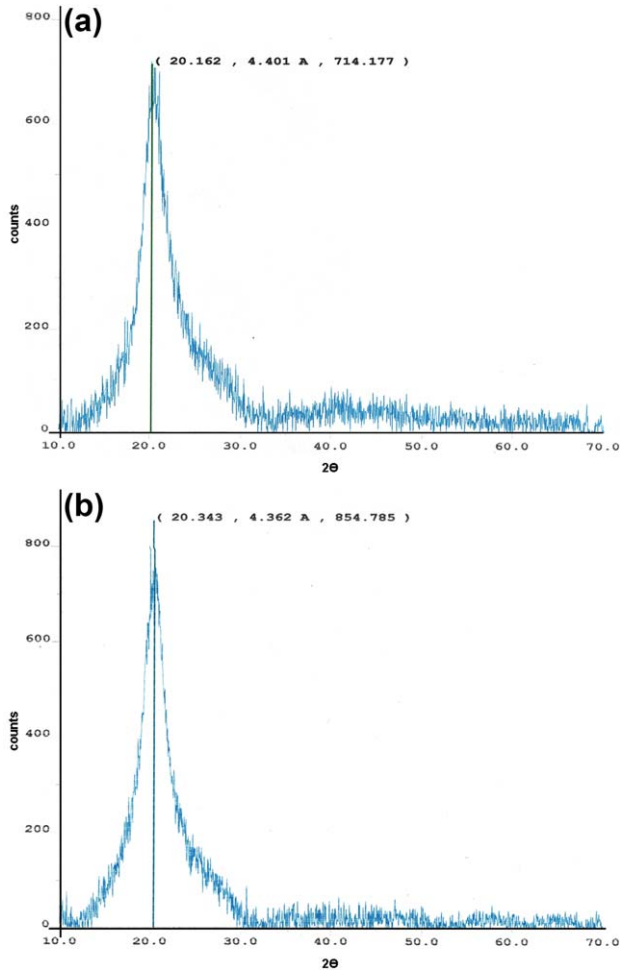


Figure 12. Examples for XRD for the chitosan synthetic polymer beads (a) without and (b) with the drug; main peak. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

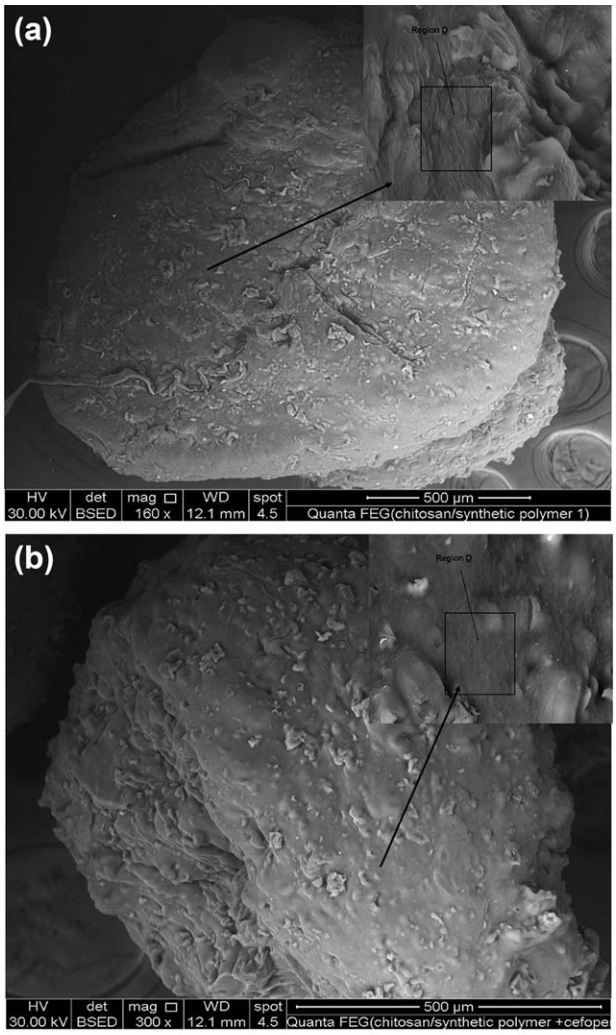


Figure 13. SEM for dry chitosan synthetic polymer beads (a) without and (b) with drug while a magnification (up to 10 times) for a certain region of each picture was placed at the corner of each one.

CONCLUSIONS

Chitosan was the most successful natural polymers in removing drugs due to the presence of nitrogen atom in its structure which enables better chance of hydrogen bond formation. Synthetic polymers contain nitrogen atoms as well have succeeded in recording powerful effect. Conversion of these polymers to beads up to 2 mm diameter has increased the chance of blending two fibers together to increase their ability to remove drugs. Wet beads enable more removal effect to pharmaceutical wastes than dry ones. Beads recycling have been studied by releasing the drug into distilled water and by applying the grinded dry beads as a blend for some types of ointment. Beads succeeded in releasing up to 9% of drug back to water. The swelling behavior of beads at different mediums and under different conditions was identified in addition to determining the water retention of beads. HPLC was the best tool to follow the drug concentration and interaction with polymers.

REFERENCES

1. Rao, M. N.; Datta, A. K. Wastewater Treatment. Oxford/IBH Publishing: New Delhi, **1987**.
2. Ferrari, B.; Paxeus, N.; Lo Giudice, R.; Pollio, A.; Garric, J. *Ecotoxicol. Environ. Saf.* **2003**, *55*, 359.
3. Sarmah, A. K.; Meyer, M. T.; Boxall, A. B. *Chemosphere* **2006**, *65*, 725.
4. Calisto, V.; Esteves, V. I. *Chemosphere* **2009**, *77*, 1257.
5. Kümmerer, K. *Chemosphere* **2009**, *75*, 417.
6. Campagnolo, E. R.; Johnson, K. R.; Karpati, A.; Rubin, C. S.; Kolpin, D. W.; Meyer, M. T.; Esteban, J. E.; Currier, R. W.; Smith, K.; Thu, K. M.; Mc Geehin, M. *Sci. Total Environ.* **2002**, *299*, 89.
7. Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T. *Environ. Sci. Technol.* **2002**, *36*, 1202.
8. Vanderford, B. J.; Pearson, R. A.; Rexing, D. J.; Snyder, S. A. *Anal. Chem.* **2003**, *75*, 6265.
9. Matamoros, V.; Bavona, J. M. *Environ. Sci. Technol.* **2006**, *40*, 5811.
10. Larsson, D. G. J.; Pedro, G.; Paxeus, N. *J. Hazard. Mater.* **2007**, *148*, 751.
11. Pedrouzo, M.; Reverté, S.; Borrull, F.; Pocurull, E.; Marcé, R. M. *J. Separ. Sci.* **2007**, *30*, 297.
12. Walsh, C. Antibiotics: Actions, Origins, Resistance; ASM Press: Washington, DC, **2003**.
13. Sanderson, H.; Johnson, D. J.; Reitsma, T.; Brain, R. A.; Wilson, C. J.; Solomon, K. R. *Regul. Toxicol. Pharmacol.* **2004**, *39*, 158.
14. Kim, S.; Jensen, J. N.; Aga, D. S.; Weber, A. S. *Chemosphere* **2007**, *66*, 1643.
15. DeSouza, S. M. L.; DeVasconcelos, E. C.; Oliveira, C. M. R. *Chemosphere* **2009**, *77*, 962.
16. Yu, D. J.; Yi, X. L.; Ma, Y. F.; Yin, B.; Zhuo, H. L.; Li, J.; Huang, Y. F. *Chemosphere* **2009**, *76*, 915.
17. Fent, K.; Weston, A. A.; Caminada, D. *Aquat. Toxicol.* **2006**, *76*, 122.
18. Abou Zeid, A. A.; El-Fouly, M. Z.; El-Zawahry, Y. A.; El-Mongy, T. M.; Abd El-Aziz, A. B. *J. Appl. Sci. Res.* **2008**, *4*, 975.
19. Garas, G. L.; Allam, M. E.; Ragab, A. Waste Management and the Environment IV 2008, DOI: 10.2495/WM080451.
20. Ahmed, A. E.-S. I.; Cavalli, G.; Bushell, M. E.; Wardell, J. N.; Hay, J. N. *Cellulose* **2012**, *19*, 209.
21. Ahmed, A. E.-S. I.; Cavalli, G.; Bushell, M. E.; Wardell, J. N.; Pedley, S.; Charles, K.; Hay, J. N. *Carbohydr. Polym.* **2013**, *92*, 1934.
22. Ahmed, A. E.-S. I.; El-Masry, A. M.; Saleh, A.; Nada, A. *Pigment Resin Technol.* **2013**, *42*, 68.
23. Mansour, A.; Srebric, J.; Burley, B. J. *J. Appl. Sci. Res.* **2007**, *3*, 1571.
24. Suramaythangkoor, T.; Gheewala, S. H. *Appl. Energy* **2010**, *87*, 128.
25. Gad, H. M. H.; El-Sayed, A. A. *J. Hazard. Mater.* **2009**, *168*, 1070.
26. Gad, H. M. H.; El-Mouhty, N. R. A.; Aly, H. F. *Separation Sci. Technol.* **2009**, *44*, 681.
27. Camarillo, R.; Pérez, Á.; Cañizares, P.; De Lucas, A. *Desalination* **2012**, *286*, 193.
28. Shawky, H. A.; Chae, S. R.; Lin, S.; Wiesner, M. R. *Desalination* **2011**, *272*, 46.
29. Tikhonov, V. E.; Stepnova, E. A.; Babak, V. G.; Yamskov, I. A.; Palma-Guerrero, J.; Jansson, H. B.; Lopez-Llorca, L. V.; Salinas, J.; Gerasimenko, D. V.; Avdienko, I. D.; Varlamov, V. P. *Carbohydr. Polym.* **2006**, *64*, 66.
30. George, P.; Nikolaos, B. *Int. J. Pharm.* **2006**, *323*, 34.
31. Helmy, S. A.; Abou-State, M. A. *Polym. Degrad. Stabil.* **1993**, *41*, 245.
32. Ahmed, A. E.-S. I.; Hay, J. N.; Bushell, M. E.; Wardell, J. N.; Cavalli, G. *J. Appl. Polym. Sci.* **2010**, *116*, 2396.
33. Ahmed, A. E.-S. I. *J. Appl. Polym. Sci.* **2011**, *122*, 1162.
34. Ahmed, A. E.-S. I. *J. Appl. Polym. Sci.* **2012**, *123*, 1889.
35. Ahmed, A. E.-S. I.; Hay, J. N.; Bushell, M. E.; Wardell, J. N.; Cavalli, G. *React. Funct. Polym.* **2008**, *68*, 1448.
36. Ahmed, A. E.-S. I.; Cavalli, G.; Bushell, M. E.; Wardell, J. N.; Pedley, S.; Charles, K.; Hay, J. N. *Appl. Environ. Microbiol.* **2011**, *77*, 847.