Sustained Release of Iodine from a Polymeric Hydrogel Device for Water Disinfection

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ABSTRACT: 2-Hydroxyethyl methacrylate (HEMA) based polymeric hydrogels were synthesized by free-radical redox bulk polymerization technique using 1% ethyleneglycol dimethacrylate (EGDMA) as crosslinking monomer and ammonium persulfate (APS) and *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine (TEMED) as redox initiator. Polymeric hydrogel samples were loaded with solid elemental iodine. Thermal and physical characteristics of polymer before loading and after 3 months release of iodine were evaluated by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). On immersing in water, different forms of iodine were released from the hydrogel device. The amount and rate of release of I^- and I_3^- were measured by analytical techniques. Released iodine species showed broad spectrum antimicrobial properties and release was sustained for about 120 days. Polymeric hydrogel iodine-based system developed can be used as a device for controlled release of iodine species at concentration levels sufficient for disinfection to get potable water. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3334–3340, 2007

Key words: crosslinking; differential scanning calorimetry (DSC); hydrogels; UV–vis spectroscopy; radical polymerization

INTRODUCTION

Disinfection of drinking water continues to be a challenging problem and more so in developing countries. About 70% of all illnesses are related to water contamination, with major diseases like cholera, dysentery, and gastroenteritis being water borne. Iodine and iodine-based compounds have been in use for medical applications for a long time as the germicidal property of iodine has been known for more than 150 years. However, use of iodine for disinfection of water has been practiced essentially under special circumstances. Impetus to the use of iodine for water treatment came in early 1920s when it was suggested that small amounts of this can be added to water to prevent goiter.[1] It is reported that iodine was used to disinfect drinking water for troops in France during First World War.[2] Subsequently, US army, during Second World War, used Globalin (tetraglycine hydroperiodide) tablets. Since 1950s numerous reports have been published on disinfection efficiencies of various forms of iodine.[3–6] More recently, iodine-based disinfection has been used by NASA in space flights. Compounds of iodine have been tried for more regulated release of iodine. These include the following: (a) organic iodide compounds, e.g., bisglycine hydroiodide, potassium tetraglycinetriodide, etc. (b) iodophors, a combination of iodine with solubilizing compounds (nonionic surfactants)[7] (c) other iodine release systems[8–12] such as iodine-incorporated resins, which release disinfecting levels of iodine. Disinfection of potable water and swimming pool water[13] by iodine has been studied against many microorganisms. It was found to be a good disinfectant except against few microorganisms like *Legionella* bacteria and some fungi.[14]

Antimicrobial properties of iodine-containing compound are due to controlled release of I_2, I^-, I_3^-, and HOI. On the basis of solution studies of iodine by UV–vis spectrophotometry, Gazda et al.[15] reported four distinct peaks in the volumetric iodine spectrum, which are indicative of three different iodine species formed after hydrolytic disproportionation in aqueous solution. The highest energy peak (226 nm) is from I^-, the two intermediate peaks (290 and 350 nm) are from I_3^-, and the lowest energy and weakest peak (460 nm) reveals the presence of I_2. Out of the four species I_2, I^-, I_3^-, and HOI obtained in aqueous iodine solutions, the I_2 and HOI have higher level of biocidal action.[16] Chang[5] indicated that I_2 shows

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more cysticidal effect when compared with that of HOI and I_3^-. The cysticidal efficiency of HOI is half of I_2 and that of I_3^- is 1/8th of I_2. Wyss and Strandskov[6] found pronounced reduction in the effectiveness of iodine at pH 9. It has been shown that the biocidal activity correlates with oxidizing capability of the species.[16] An enzyme-based iodine (EBI) disinfectant system was developed by Duan et al.[17] which continuously generates free molecular iodine in a controlled fashion and was evaluated for use in disinfecting flexible fiberoptic endoscopes. Kawai and Sugiura[10] have developed iodine-containing articles for controlled release of iodine gas and studied them for disinfection. A triodide polymer membrane based on a blend of polystyrene and polyethylene has also been evaluated against *Escherichia coli* for disinfection of water. It was seen that release of iodine at the ppm level did not exceed the experimentally determined oral and intravenous doses of iodine from the membrane and was sustained for a prolonged period of time as measured by ion-selective electrode.[18]

The present study involves synthesizing a polymeric hydrogel device for sustained release of various iodine species into water for a prolonged period of time and evaluation of their microbiocidal efficiency for water disinfection.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA), ammonium persulfate (APS) of reagent grade were from CDH, India and used as-received. *N,N,N′,N′*-tetramethyl ethylenediamine (TEMED), ethyleneglycol dimethacrylate (EGDMA), resublimed iodine, and sodium iodide (E. Merck, Germany) were reagent grade chemicals and were used as-received. Luria agar and peptone (bacteriological grade) for microbiological assay were obtained from Hi-Media Laboratories, Mumbai, India and were used for antimicrobial studies. *E. coli* ATCC 25922 (Gram negative) and *Staphylococcus aureus* ATCC 33807 (Gram positive) were obtained from Department of Chemistry, IIT Delhi, India for antimicrobial assessment of iodine released from polymeric hydrogel.

Polymerization

HEMA was polymerized with different percentages (0–5%) of EGDMA as crosslinker by a redox initiator (APS 0.6%, TEMED 0.6% of the total monomer concentration) in an aqueous solution. Poly(HEMA) containing only 1% EGDMA was selected for release of iodine because on further increasing the amount of crosslinker in the monomer mixture, the hydrogel becomes brittle and crack formation was also observed. The final formulation consisted of HEMA (99%), EGDMA (1%), and distilled water (8%). The reaction mixture was then poured into a polypropylene mold with an inner diameter of 12.2 mm and a tubular hole was created by inserting a 6.1 mm solid teflon rod into the mold during polymerization. Within time span of 5–20 min a polymeric tube was obtained. All the sample tubes were prepared in the same mold to maintain homogeneity. Polymeric tubes thus formed were immersed into distilled water at room temperature for 24 h to remove unreacted monomers, and then dried to constant weight at room temperature for characterization and other studies.

Polymer characterization

Attenuated total reflectance-Fourier transform infrared spectroscopy

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of crosslinked poly(HEMA) before loading and after 3 months release of iodine were recorded on a Perkin–Elmer spectrum one spectrometer.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) studies of various polymeric samples were carried out using Perkin–Elmer DSC-7 system. Vacuum-dried samples were loaded into the DSC system and the thermogram was run in the temperature range of 0–200°C under the nitrogen atmosphere at the heating rate of 10°C/min.

Scanning electron microscopy

The surface characteristics of synthesized crosslinked polymer before loading and after 3 months release of iodine was studied using Stereoscan 360 (Cambridge Scientific Industries, UK) scanning electron microscope, after coating the samples with silver.

Swelling studies

Water absorption capacities of various hydrogels were determined by immersing samples for 24 h in distilled water at room temperature. The weights of the swollen devices were determined at various time intervals after blotting out the excess adhering water from the device with filter paper for 10 s. The experiment was carried out in duplicates. The percent swelling of the hydrogel device was then calculated from the equation:

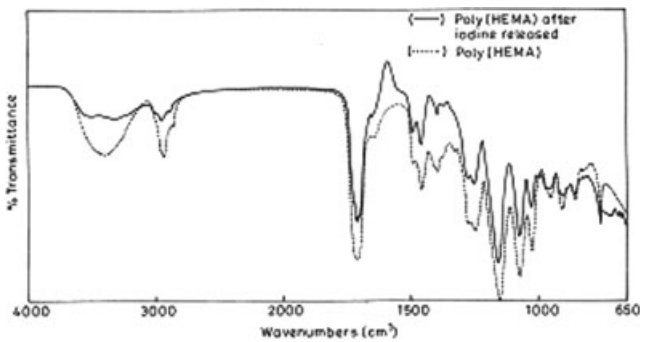

Figure 1 ATR-FTIR spectra of (a) poly(HEMA) and (b) poly(HEMA) after iodine release.

$$\% \text{ swelling} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s and W_d are the weights of the hydrogel devices in the swelled and dry states.

Release of iodine from polymeric hydrogel devices

Aqueous iodine solution (pH 5.8) and different iodine forms I^- (NaI, 0.05*N*), I_3^- (NaI-I_2, 0.05*N*), OI^- (I_2 solution at pH 10.0) were prepared in water and their UV–vis scan were taken from 260 to 800 nm using Perkin–Elmer spectrophotometer for determining the maximum absorption of various iodine species. Poly(HEMA)-based hydrogel device with 1% EGDMA was used for release pattern of iodine with water as surrounding medium after filling the device (6.1 mm inner diameter and 6 cm length) with 1 g of resublimed iodine. Iodine released into water from the polymeric hydrogel was scanned by UV–vis spectrophotometer. The release was studied into 100 mL distilled water which was replaced with fresh 100 mL distilled water after 24 h. Experiments were carried out in duplicates. The release pattern was studied at room temperature (30°C) upto 3 months using UV–vis spectrophotometer and iodine-selective ion meter and was also compared with the standard curves of I^- and I_3^- for determining the species and their concentrations in the aqueous solution. The estimation of remaining iodine left in polymer after the release studies of 3 months was checked by X-ray fluorescence (Minipal PW 4025 Philips) which helps to calculate the percentage of residual iodine in the polymer.

Evaluation of antimicrobial properties of released iodine

Polymeric hydrogel devices filled with 1 g iodine were immersed into 100 mL of contaminated water with viable cell count of 1×10^5 cfu/mL of *E. coli*. After different intervals of time (0, 10, 30, 60 min), 1 mL of aliquots were taken out from the surrounding media, serially diluted, and spread onto the Luria agar plate and left in an incubator at 37°C for 24 h. The next day, plates were observed and bacterial colonies if present were counted using a colony counter.[19] The released iodine was also tested against *S. aureus* (Gram positive) under similar conditions.

RESULTS AND DISCUSSION

ATR-FTIR spectroscopy

The ATR-FTIR spectra of poly(HEMA) before loading and after release of iodine are presented in Figure 1. The poly(HEMA) showed characteristic peaks of —OH at 3399 cm^{-1}, —C=O at 1714 cm^{-1}, —C—O of carbonyl at 1200 cm^{-1}, —C—O—C stretching at 1022 cm^{-1}, and peak of —C=C at 1637.13 cm^{-1} of the monomer was absent, indicating complete polymerization. Additional peaks at 747 and 900 cm^{-1} due to iodide groups were observed in the spectrum of polymer sample taken after release of iodine. This confirmed that some of the elemental iodine has been incorporated onto polymeric surface probably because of chemical interaction of iodine with hydroxyl group of poly(HEMA).

Differential scanning calorimetry

The DSC thermograms of crosslinked poly(HEMA) before loading and after release of iodine are presented in Figure 2. It was found that T_g of polymer decreased from 99°C to 70°C due to the incorporation of iodine into the polymeric matrix.

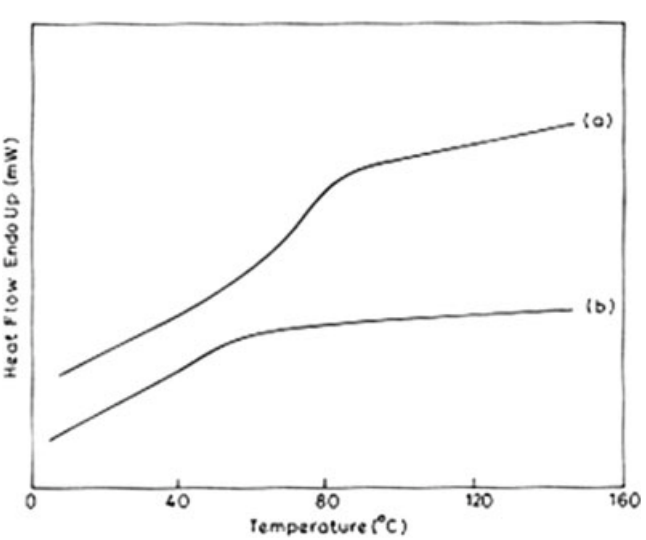

Figure 2 DSC thermograms of (a) poly(HEMA) and (b) poly(HEMA) after iodine release.

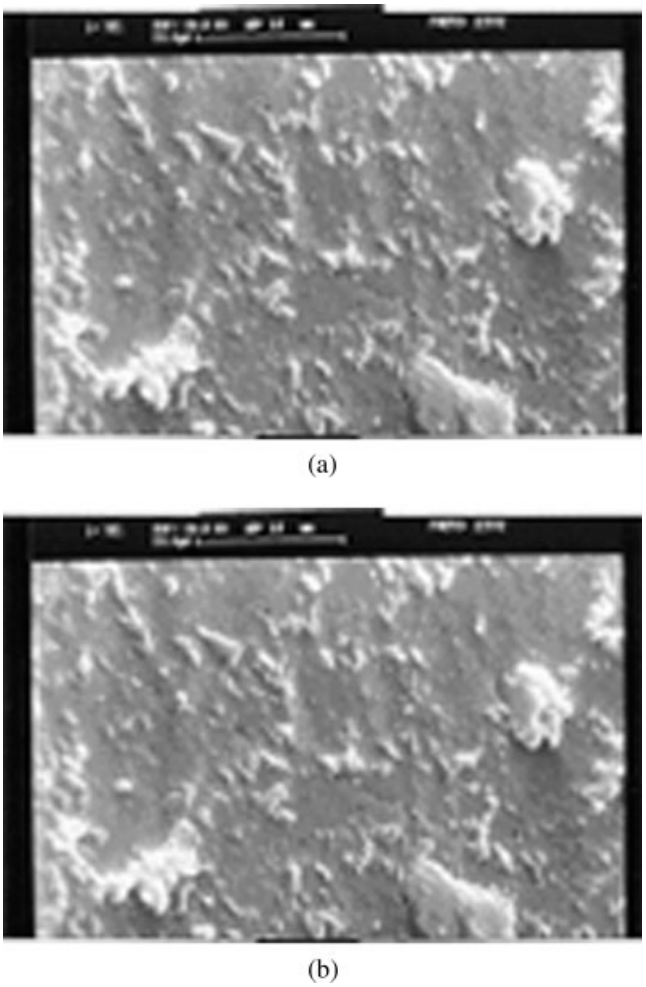

Figure 3 SEM photographs of (a) poly(HEMA) and (b) poly(HEMA) after iodine release.

Scanning electron microscopy

The surface structures of the crosslinked poly (HEMA) before and after the release of iodine were studied by scanning electron microscopy (SEM) in the vacuum-dried state. The crosslinked poly (HEMA) showed uniformly smooth surface [Fig. 3(a)] while the surface of polymer sample after 3 months release of iodine showed a shrunken structure with random holes due to the release of iodine from the system [Fig. 3(b)].

Swelling studies

Plot of % swelling versus no. of days of poly(HEMA) containing 1% EGDMA is shown in Figure 4. Percentage swelling which is due to water absorption by polymer, increased with number of days. After 10 days, percentage swelling becomes constant ($\sim$ 35%) as it reaches a plato corresponding to maximum absorption of water by polymer.

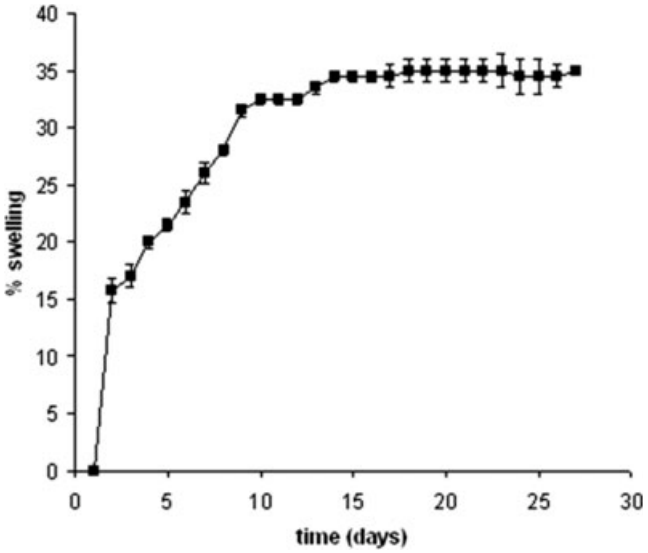

Figure 4 Swelling studies of poly(HEMA) crosslinked with 1% EGDMA at 32–34°C.

Release of iodine from polymeric hydrogel device

UV–vis spectra of standard stock solution of I^-, I_3^-, OI^-, and aqueous iodine solution are shown in Figure 5. UV–vis spectra of aqueous iodine solution showed the peak of I^- (225 nm), I_3^- (285 and 351 nm), I_2 (460 nm) as expected from the two equilibriums [eqs. (1) and (2)]. All these peaks were also observed in iodine-loaded poly(HEMA) system except the peak of I_2 at 460 nm, probably because its concentration is too low to be detected by UV spectrophotometer. Per

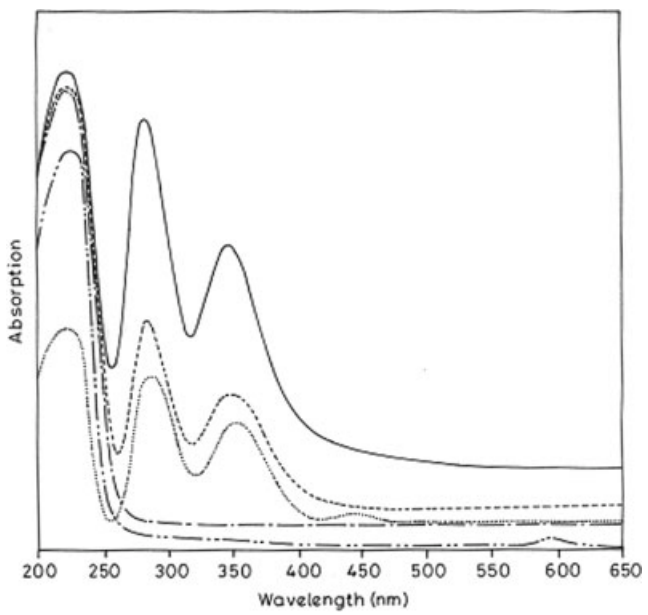

Figure 5 UV–vis spectra of standard stock solution of I_3^- (—), I^- (-·-), OI^- (-··-), aqueous iodine solution (···), and released iodine from the polymer (—).

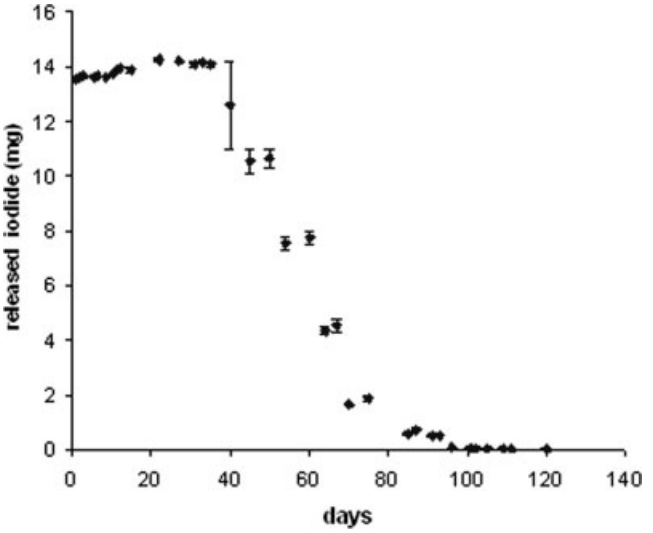

Figure 6 Release of iodide (I^-) from poly(HEMA) measured by iodide-selective ion meter.

day iodine released from the polymeric hydrogel device in the form of I^- and I_3^- over a period of 3 months is depicted in Figures 6 and 7, respectively. It was seen that I^- maintains a constant release of $\sim$ 14 mg per day upto 40th day and then decreased with time to a level of 1 mg on 90th day. However, a constant release of I_3^- of $\sim$ 0.31 mg per day was observed for upto 96 days and then gradually decreased with time to 0.05 mg on 120th day.

All the iodine species could not be detected by UV–vis spectrophotometer. However, quantitative estimation of various iodine species released in aqueous solution from polymeric hydrogel device could be estimated from the K_1 and K_2 values corresponding to eqs. (3) and (4). The concentrations of I_2

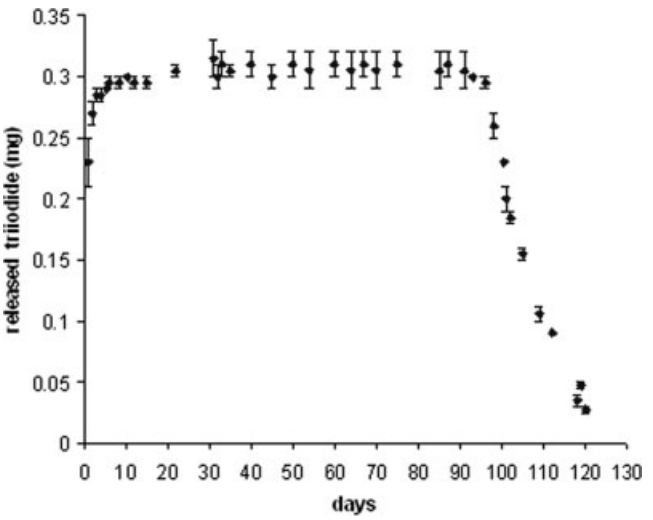

Figure 7 Release of triiodide (I_3^-) from poly(HEMA) measured by UV spectrophotometer.

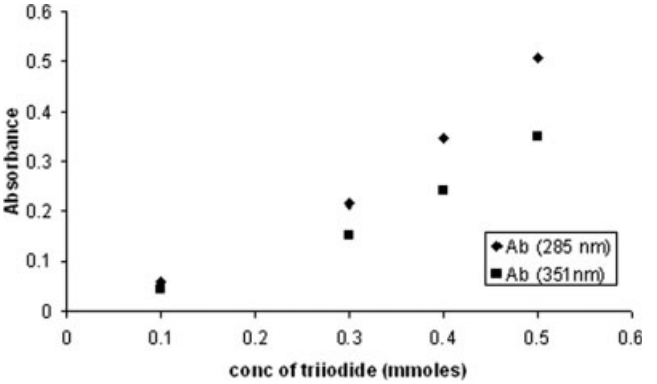

Figure 8 Lambert–Beer curve of triiodide at wavelength 285 and 351 nm using sodium iodide and iodine.

and HOI species were determined by the following equilibriums:

$$I_2 + H_2O \Leftrightarrow HOI + I^- + H^+ \quad (1)$$

$$I_2 + I^- \Leftrightarrow I_3^- \quad (2)$$

$$K_1 = \frac{[HOI][H^+][I^-]}{[I_2]\ [H_2O]} \quad (3)$$

$$K_2 = \frac{[I_3^-]}{[I_2]\ [I^-]} \quad (4)$$

The procedure adopted for estimation of I_2 and HOI was as follows. If a is the amount of I_2 taken initially at equilibrium, remaining $I_2 = a - (x + x')$, where x is the amount of HOI and I^- formed as per eq. (1)

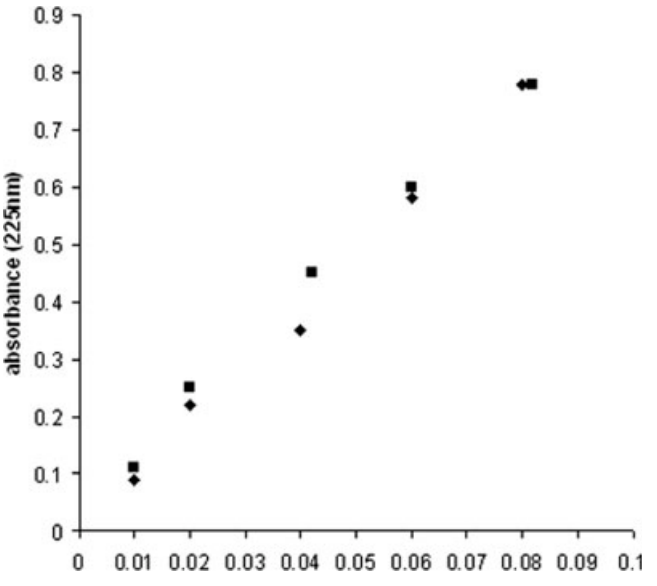

Figure 9 Lambert–Beer curve of standard sodium iodide solution concentration determined gravimetrically (■) and by iodide-selective iodide ion meter (◆).

TABLE I
Concentration of Iodine Species and Calculated Values of Equilibrium Constants

I_2 (mmol) a and $[a - (x + x')]$	I^- (mmol) $(x - x')$ By ion meter	I^- (mmol) $(x - x')$ By Lambert–Beer (Fig. 9)	I_3^- (x') (mmol) Lambert–Beer (Fig. 8)	HOI (x) (mmol) $(I^- + I_3^-)$	K_2 (L/mol)	K_1 (10^{-12}) (mol^2/L^2)
0.6 (0.399)	0.124	0.1024	0.049	0.1514	1197	3.8
0.8 (0.5)	0.142	0.138	0.081	0.219	1173	6.0
1.0 (0.588)	0.172	0.168	0.122	0.29	1230	8.1
1.2 (0.683)	0.19	0.1963	0.1609	0.356	1200	10.0
1.4 (0.77)	0.22	0.214	0.206	0.42	1243	10.0
1.6 (0.8414)	0.24	0.236	0.2612	0.497	1314	13.9

and x' is amount of I_3^- formed as per eq. (2). Thus, it is seen that HOI $= x$, $I^- = x - x'$ and $I_3^- = x'$.

For any given solution of I_2, amount of I_3^- (x') was directly estimated from Lambert–Beer curve (Fig. 8). I^- $(x - x')$ was calculated from Lambert–Beer curve (Fig. 9) and also by direct measurement using an iodide-selective ion meter. HOI was estimated as equivalent to I^- plus I_3^-. Concentration of different species of I_2 at equilibrium is shown in Table I. In parenthesis in column 1 the equilibrium concentration of I_2 is equivalent to $[a - (x + x')]$ and is shown along with the initial amount (a) of I_2 taken. The equilibrium constant K_2 was found to be 1.2×10^3 L mol^{-1} and K_1 was found to be 4–10 $\times$ 10^{-12} mol^2 L^{-2} at pH 5.8 and were used to calculate I_2 and HOI released from the polymeric hydrogel device.

The cumulative amount of iodine released from the polymeric hydrogel device over the entire period of 3 months was found to be 0.65 g as iodide (I^-) and 0.03 g as triodide, as calculated from Figures 8 and 9. The equilibrium constants K_1 (10×10^{-12} mol^2 L^{-2}) and K_2 (1.2×10^3 L mol^{-1}) were used to calculate the cumulative amount of iodine released in the form of HOI and I_2 and were found to be 0.004 and 0.132 g respectively, at pH 5.8. Thus there should be a balance of about 0.18 g of iodine remaining incorporated in the polymer. This was further confirmed by X-ray fluorescence (XRF) which showed about 3% of iodine (0.15 g iodine) left in the tube wall after 3 months release studies.

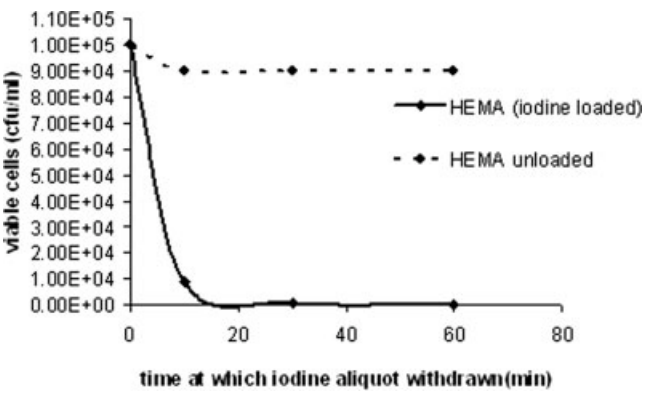

Figure 10 Antimicrobial activity of released iodine against *Escherichia coli*.

Antimicrobial properties of released iodine

Figure 10 shows antimicrobial activity of released iodine from polymeric hydrogel device against *E. coli*. It was observed that bacterial colony decreased with time as the cumulative amount of iodine released from the polymeric hydrogel device increases with time. The cumulative amount of iodide (I^-) released in 10 min was found to be about 1 ppm (7.8×10^{-3} mmol) as measured by iodide-selective ion meter and I_3^- was 0.049×10^{-3} mmol as measured by UV spectrophotometer. HOI and I_2 concentration at pH 5.8 was calculated from eqs. (3) and (4) taking K_1 and K_2 value as 10×10^{-12} mol^2 L^{-2} and 1200 L mol^{-1}, respectively. Iodine present in the form of HOI and I_2 was found to be of 4.47×10^{-3} mmol/L and 5.23×10^{-3} mmol/L, respectively. I_2 concentration was found to be nearly 1 ppm which is too low to be detected by UV spectrophotometer. However, as per literature reports I_2 has significant antimicrobial property even at 1 ppm.[16] Therefore, significant bactericidal action is probably due to I_2 and HOI. Although bactericidal properties of I_3^- and I^- are feeble, they also contribute in bactericidal action due to prolonged and high percentage release from the polymeric hydrogel. This is in agreement with literature on the efficiency of bactericidal nature of various iodine species.[16]

CONCLUSIONS

The poly(HEMA)-based iodine delivery system designed showed controlled release of iodine species over several months at ppm levels sufficient for disinfection to get potable water.

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