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Preparation of Novel Hydrogel Composites with Enhanced Properties for Environment, Medical and Engineering Applications

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Abstract

Hydrogels composite (HGC) based on the crosslinking of maleic acid (MA) with hydroxypropyl methyl cellulose (HPC) and poly (vinyl alcohol) (PVA) were prepared. Three type of networks were designed in different ratio of PVA, CMC and MA. 100/100/100 (HGC-1), 50/50/100 (HGC-2) and 25/25/100 (HGC-3) (wt/wt/wt%) compositions of PVA, CMC and MA were used to prepare cross-linked composites materials. Variation of the crosslinking ratio of –COOH and –OH groups lead to new macromolecular supports with each composition. Thermal analyses [differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)], and Fourier transform infrared spectroscopy (FTIR) were employed to characterize the HGC. and reveal the structural properties of such composite materials. Variations in the glass transition temperature (Tg) of composite materials indicating the different thermal properties of each composites. In addition, the changes in the melting temperature (Tm), shape and area attributed to the different degrees of crystallinity of each composites. Studies were made on swelling behavior for all prepared composites using deionized water. The obtained results indicated that the swelling ratio of hydrogel decreased by increasing the concentration of MA. Removal of methylene blue from aqueous solution with each composite material was studied using UV-visible spectroscopy at pH 6. Dye adsorption on composite (HGC-3) was found maximum. Maximum uptake capacity was assumed to occur through the complexation and electrostatic interaction between composite and dye. Finally, macromolecular support of each composite materials were used to include and release paracetamol drugs in a sustainable way using phosphate buffer solution of pH 7.4. Complete adsorption of paracetamol onto the HGC materials was confirmed from UV-visible spectrum.

Keywords: HPC/PVA/MA composite; cross-linked network; dye adsorption and drugs release

Introduction

Hydrogel composites (HGCs) as promising materials are of greatest significance in the biomedical

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fields and have been most extensively studied in academic and industrial research such as biomimetic, biosensors, artificial muscles, chemical separation, biomaterials, cell culture systems, catalysis, photonics, drug delivery systems and separation purpose due to the remarkable characteristics, such as flexibility and versatility in fabrication, variety in composition, high tunability in the physical, chemical, and biological properties, high moldability in shape, especially their excellent biocompatibility.

Poly (vinyl alcohol) (PVA) is an attractive synthetic polymer hydrogel due to its good biocompatibility has been applied in several advanced biomedical applications e.g. wound dressing, wound management, drug delivery systems, artificial organs, and contact lenses. But, PVA hydrogel possesses insufficient elasticity, stiff membrane, and very limited hydrophilicity which restrict its uses alone.

Hydroxypropyl methylcellulose (HPMC) is a semi synthetic polymer of most abundant naturally occurring biopolymer, cellulose that has excellent film forming capability, superior tensile strength, biocompatibility and biodegradability. It possesses good swelling behavior and accelerates the wound healing process by keeping the environment moist. It is soluble in both water and polar organic solvents, making it possible to use both aqueous and non-aqueous media. HPMC is most commonly used in the food industry as a stabilizing agent, as a protective colloid, as a thickener and as an emulsifier. However, HPMC films have moderated mechanical strength and are resistant to oils and fats, flexible, transparent, odorless, and tasteless. So, the water sensitivity of HPMC films, which produces a loss of barrier properties or even a solubilization into foods with high water activities, prevents their industrial applications. The addition of synthetic polymers such as PVA to HPMC hence gives us a blend with superior and desired properties because both polymers are compatible with each other and form miscible blends when blended together. In addition to that the incorporation of PVA in certain macrogel or nanogel ensures its excellent mechanical strength, and the chemical crosslinking is needed to create and modify polymer nanostructure, to improve thermal, mechanical and chemical stabilities. PVA content in the gels type gives higher affinity to crosslink formation through the intra- and or intermolecular hydrogen bonding via H groups. To know this fact, we have chosen HPMC and PVA as the polymer matrix in the present study to get combined effect of both polymers on the final properties of nanocomposites.

Wu et al. have prepared ternary blend films with different ratios of starch/ PVA/citric acid that films can be used as an active food packaging system due to their strong antibacterial effect. It has also been reported that dicarboxylic acids such as citric acid maleic acid (MA) etc. can act as a crosslinking in methylcellulose based hydrogels due to the presence of carboxyl groups in the structure which form hydrogen bonds with –OH in the PVA.

Hence, MA reinforced nanocomposites with biodegradable and biocompatible polymers and nano-fillers can combine the ductile properties of a polymer matrix and high strength of nano-fillers. This is mainly due to the presence of oxygen-containing functional groups in the structure of MA, which improve interfacial interaction between MA and the polar polymer matrix.

However, hydrogel composites based on HPMC, PVA and MA was not found in the literature studied so far. Therefore, the purpose of this study was to prepare hydrogel composites based on the cross-linking of PVA/HPMC/MA. Then, these composite materials are characterized by thermal analyses differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and Fourier transformed infrared spectroscopy (FTIR). They were performed to evaluate the dye adsorption properties for methylene blue (MB) from aqueous solution. In addition to that, each

composite material was explored to include and release paracetamol drugs in a sustainable way using phosphate buffer solution of pH 7.4.

Materials

PVA molecular weight ≈115000 and maleic acid were purchased from Loba Chemical Com. HPMC was purchased from Chem Cruz. All the chemicals used for this study were research grade and used as received.

Synthesis of chemically cross-linked hydrogel composite (HGC)

Solution method was used to obtain HGC. To prepare HGC blending of PVA, HPMC and MA were done as follows:

Table I. Composition of PVA, HPMC and MA for hydrogel formation

Sample No	Raw materials ratio (%wt/wt/wt)		
	Polyvinyl alcohol (PVA)	Hydroxypropyl methyl cellulose (HPMC	Maleic acid (MA)
HGC-1	50	50	100
HGC-2	100	100	100
HGC-3	25	25	100

The weighted amount of PVA, HPMC and MA were taken in a beaker. Then 30 mL deionized water was added to it. Afterwards, the solution was sonicated for 30 mins at 50 °C. The solution was then cast onto petri dish. Then the crosslinking of the solution was obtained by thermal treatment in the oven at 120°C for 6 hours. Cross-linked films were then peeled off and transferred into vial.

FTIR analysis

FTIR is used to analyze the presence of functional groups of prepared composite materials. Characterization was carried out using IRTracer-100 of Shimadzu Corporation, Japan. Characteristics bands –C=O, -C-O, -O-H, of the prepared composites ware mainly identified by using FTIR technique. For each the prepared composite materials a pellet was prepared using KBr. Then the pellet was mounted and adjusted on sample surface. Afterwards, a black gripper was used to cover the sample surface. A computer based FTIR program was used to identify the functional groups of the prepared composite materials. The entire FTIR spectrum of the prepared sample has been recorded in the range of 500 to 4000 cm^{-1}.

TGA analysis

TGA experiments were performed for the prepared hydrogel composites. The weight loss of the sample was recorded by using TGA-550 Shimadzu Corporation, Japan. The prepared Hap-NPs were placed in a TGA sample pan. Sample masses were confirmed with a precision balance. A computer based TGA program was used for obtaining TGA curve. The samples were held at room temperature under a flow of nitrogen gas to create inert environment for the sample and drive off gases such as oxygen, water vapor. Then the temperature was increased from room temperature to 600 °C at a rate of 10 °C/min. At the end of each experiment the temperature was held constant at 600 °C for ten

minutes. After ten minutes the gas flow was switched off and waited until the temperature cooled down to room temperature.

Swelling property

Swelling degree was determined using dried hydrogel samples and distilled water as swelling agent. The dried samples of certain amount was weighed by an analytical balance and was immersed in deionized water (pH = 7) at room temperature. They kept 48 h in water bath for swelling. Afterwards, the swollen composite hydrogels were removed from water bath. Excess surface water was wiping off with filter paper and weighed carefully. The weight change for each sample was recorded. The following equation was used to determine the swelling degree.

$$\text{Swelling degree (\%)} = \{(W_{wet} - W_{dry})/W_{dry}\} \times 100 \quad (1)$$

where: W_{wet} = weight of the swelled composite at time t

W_{dry} = weight of the dried composite at time 0

Preparation of stock solutions

0.0030 g of solid dye, MB was taken in a 100.0 mL volumetric flask and de-ionized water (specific conductance < 0.1 μS cm^{-1}, obtained from Water Purification System, Model No. WDI 15, Humanlab Instrument Co., Korea) was added to it and up to the marked. Hence, 9.38 × 10^{-5} M of MB was prepared as a stock solution. Similarly, 50 mL 0.40 × 10^{-3} M of paracetamol solution was prepared as a stock solution. Further dilution was made when necessary.

Adsorption study of dyes

The ability of the hydrogels to adsorb MB from an aqueous solution was determined at room temperature. Adsorption studies have been carried out using a batch equilibrium technique.

20.0 mL 4.5 × 10^{-5} M MB solution was taken in a 50 mL reagent bottle and 0.6038 g HGC-1 was added. Then reagent bottle was placed at 25.0 °C. After different time intervals of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 24.0, 48.0, 72.0, and 96.0 hours, the clear solution from the reagent bottle was taken for spectrophotometric analysis using UV Spectrophotometer (Model No. UV-1800, Shimadzu, Japan) to determine the maximum absorbance, ca. 665 nm for cationic MB. After each experiment the clear solution was returned to the reagent bottle.

From the value of absorbance, concentration of each solution can be determined by the following equation:

$$\text{Concentration of MB} = \text{Absorbance of MB at 665 nm}/\varepsilon_{665} \quad (2)$$

The amount of dye adsorbed onto prepared hydrogels was determined by the following equation:

$$\text{Amount adsorbed} = \frac{C_1 - C_2 \times M}{1000 \times m} \times V \quad (3)$$

Where, C_1 and C_2 are the concentrations of MB at initial and equilibrium respectively, M is the formula mass of MB, V is the volume of the solution, m is the amount of adsorbent used.

Similar studies were performed for adsorption of MB on HGC-2 and HGC-3. The results obtained were summarized in Table 2, 3 and 4.

Drug release property

To conduct the drug release experiment, paracetamol was taken as a model drug and phosphate buffer solution of pH 7.4 was used as release medium. Dried HGC was loaded with drug by immersing it in aqueous solution of paracetamol (0.12 mM) for 24 h and then dried at room temperature.

20 mL of the prepared 0.12 mM drug solution was taken in each HGC. After that aliquots from the release medium were withdrawn at predetermined time intervals and analyzed by using UV Spectrophotometer at 245 nm. The removed release medium was replaced with the same volume of fresh buffer solution at the same temperature.

Results and discussion

Infrared spectral analysis has been utilized to prove the cross linking of co-polymer. For this purpose the FTIR spectra of PVA, maleic acid, HPMC and crosslinking co-polymers are shown in Figure-1(a), (b), (c) and (d), respectively.

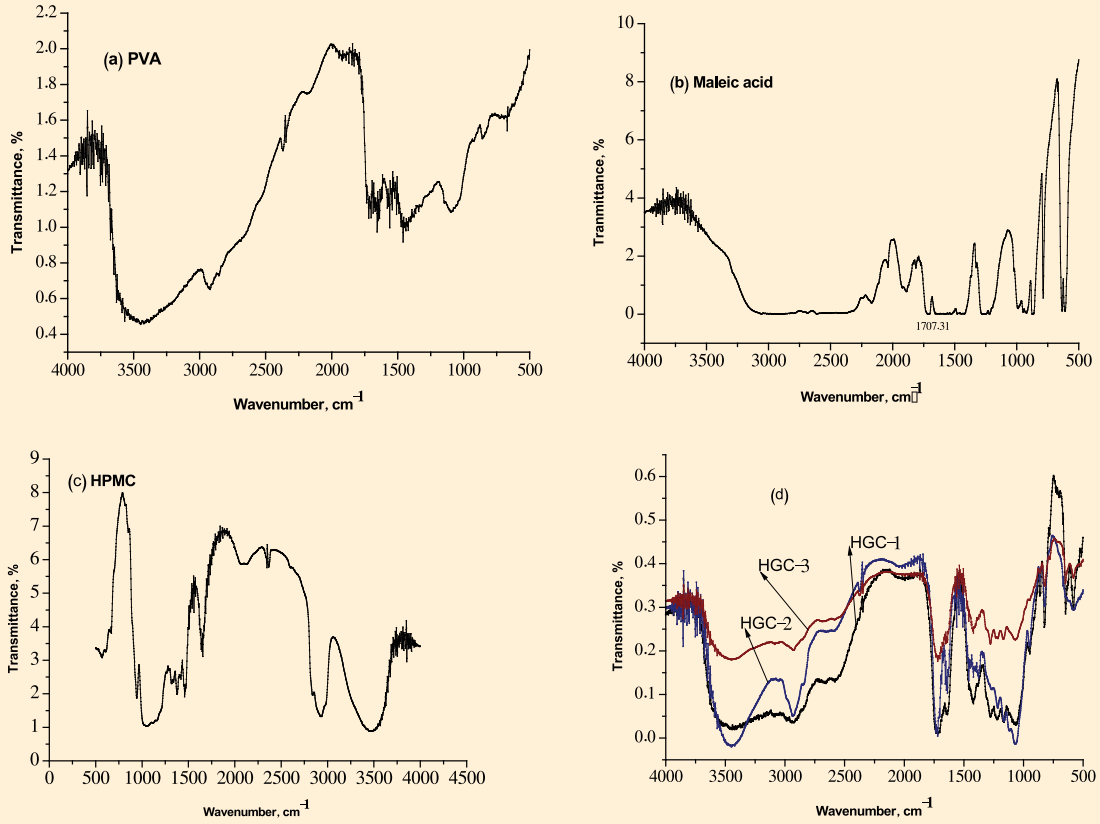

Fig. 1. (a) FTIR spectrum of PVA (b) FTIR spectrum of Maleic acid (c) FTIR spectrum of HPMC (d) FTIR spectrum of the prepared HGC

From the spectra of PVA (Figure-1(a)), it shows a band at 3415.13 cm^{-1}, due to the hydrogen bonded hydroxyl groups, 2924.51 cm^{-1} for C-H stretching, 1645.50 cm^{-1} for bending HOH and 1093.34 cm^{-1} for Out-of-plane C–O vibration. Figure-1(b) shows the spectra of maleic acid. It shows a band at

1712.62 cm^{-1} due to stretching of –CO– group of carboxylic acid. From the spectra of HPMC (Figure-1(c), shows a strong band at 3459.40 cm^{-1}, due to the stretching frequency of the –OH group. The band at 2930.90 cm^{-1} is the result of C–H stretching vibration. The band at 1639.08 cm^{-1} due to stretching of –CO– group. The bands around 1454.84 and 1371.99 cm^{-1} are assigned to $–CH_2$ scissoring and –OH bending vibration, respectively. The band at 1040 cm^{-1} is due to C–O stretching vibration.

From the (Figure-1(d) shows the cross link copolymer formation using different ratio of PVA, maleic acid and HPMC. The strong band at 1723.22 cm^{-1} for all the copolymers indicates the stretching of –CO– group of ester formation due to the cross link of one –OH group from PVA and one –COOH group from maleic acid and another –COOH group of maleic and –OH group from HPMC.

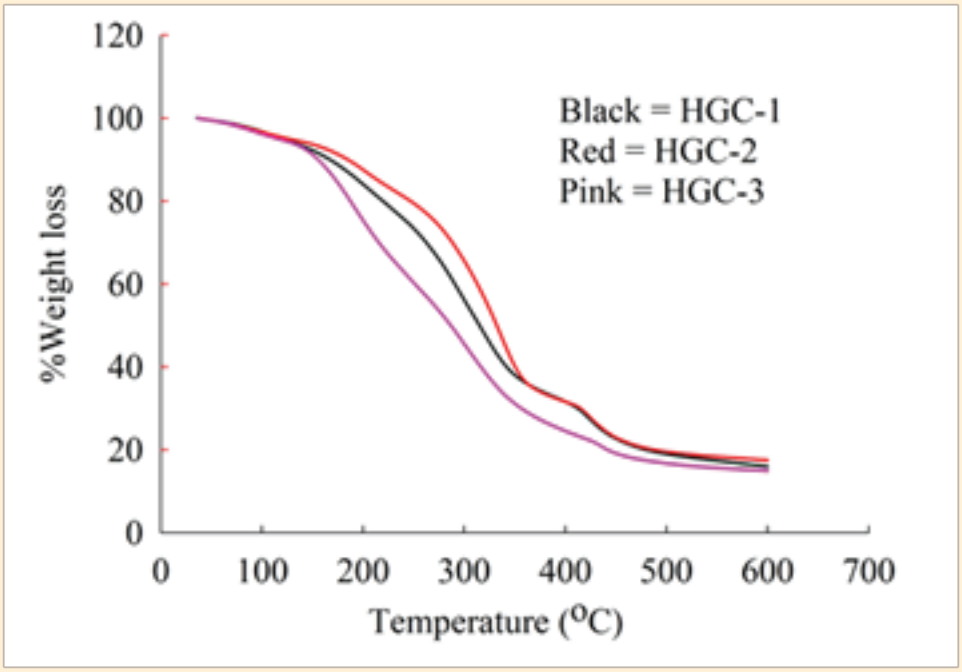

Fig. 2. Thermogram of the three prepared HGC

TGA Explanation

Thermal analysis was done to investigate the thermal stability of the prepared composite materials. Figure-2 compares the thermal stability and decomposition curves of PVA, HPMC and MA cross-linked composite materials. A weight loss before 150 °C was observed for all samples. This mass loss is related to the release of physically adsorbed water molecules. Two degradation stages were noted for each sample. First one occurred approximately between 100 to 150 °C. The mass loss of the composite material in the second step starts at 150 °C and continued until 500 °C. It is assumed that the decomposition after 150 °C is related to dehydroxylation and/or decarboxylation of HGC composite materials. Observation of the obtained thermogram clearly reveals stability variation of the prepared composite materials. Among them HGC-3 composite materials shows lowest stability. The stability of HGC-1 is in between HGC-2 and HGC-3. HGC-2 with 100/100/100 (wt/wt/wt%) composition of PVA/HPMC/MA shows the highest stability. After the required crosslinking reaction more carboxylate ions are present in HGC-3 of 25/25/100 (wt/wt/wt%) ratio of PVA/HPMC/MA. The presence of these free carboxylic groups lowers the stability of HGC-3 composite. Lowest

stability of HGC-3 composite is also related to the less crosslinking of PVA/HPMC/MA. It is noteworthy that the composite HGC-2 with 100/100/100 (wt/wt/wt%) ratio of PVA/HPMC/MA has been shown highest stability. Lowest weight loss of HGC-2 is related to the highest crosslinking of PVA/HPMC/MA. Thus, crosslinking of the functional groups have significant effect on the stability of the prepared composite materials.

*Swelling Behavior Test*_

A variation in the swelling ratio of the prepared composites as a function of %weight of PVA, HPMC and MA has been represented in Figure-3. Among the prepared composite materials HGC-2 has the highest swelling ability. HGC-1 has the lowest. The degree of swellability is correlated with the amount of maleic acid. With the high amount of maleic acid reinforcement of the composite matrix is highest. Highest reinforcement of the composite matrix yields lowest porosity. Hence, swelling ability of the composite matrix decreased.

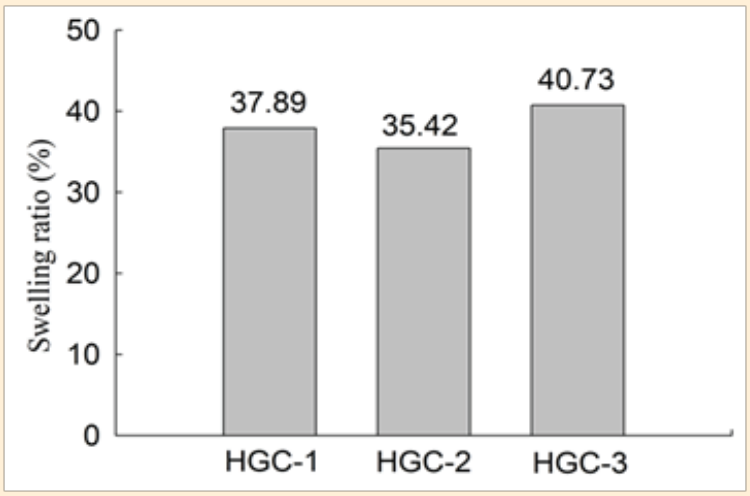

Fig. 3. Comparative swelling behavior of three different HGC

Adsorption of MB onto hydrogels

The study of adsorption of MB on different forms of hydrogels was performed. The results obtained are shown in Table 2, 3 and 4.

Table II. Determination of equilibrium time for adsorption of MB on HGC-1[a]

Time/h	Absorbance (at 665 nm)	Amount Adsorbed (mg/g)
0.0	3.202	0.0
0.5	2.602	0.129
1.0	1.713	0.319
1.5	1.366	0.394
2.0	1.085	0.455
2.5	0.986	0.475
3.0	0.854	0.504
4.0	0.739	0.529
24.0	0.397	0.601
72.0	0.297	0.623

[a]Total volume of solution = 30.0 mL, initial concentration of MB = 4.5×10^{-5} M, amount of HGC-1 = 0.6038 g

Table III. Determination of equilibrium time for adsorption of MB on HGC-2[a]

Time/h	Absorbance (at 665 nm)	Amount Adsorbed (mg/g)
0.0	3.202	0.0
0.5	1.875	0.280
1.0	1.833	0.289
1.5	1.701	0.317
2.0	1.609	0.336
2.5	1.595	0.339
3.0	1.588	0.340
4.0	1.580	0.342
24.0	0.640	0.540
72.0	0.539	0.561

[a]Total volume of solution = 30.0 mL, initial concentration of MB = 4.5×10^{-5} M, amount of HGC-2 = 0.6139 g

Table IV. Determination of equilibrium time for adsorption of MB on HGC-3[a]

Time/h	Absorbance (at 665 nm)	Amount Adsorbed (mg/g)
0.0	3.202	0.0
0.5	2.477	0.156
1.0	1.402	0.387
1.5	1.054	0.462
2.0	0.762	0.524
2.5	0.563	0.567
3.0	0.464	0.587
4.0	0.351	0.613
24.0	0.126	0.661
72.0	0.114	0.664

[a]Total volume of solution = 30.0 mL, initial concentration of MB = 4.5×10^{-5} M, amount of HGC-3 = 0.6022 g

Here, the respective UV-adsorption spectrum of methylene blue dye using HGC-3 is shown below:

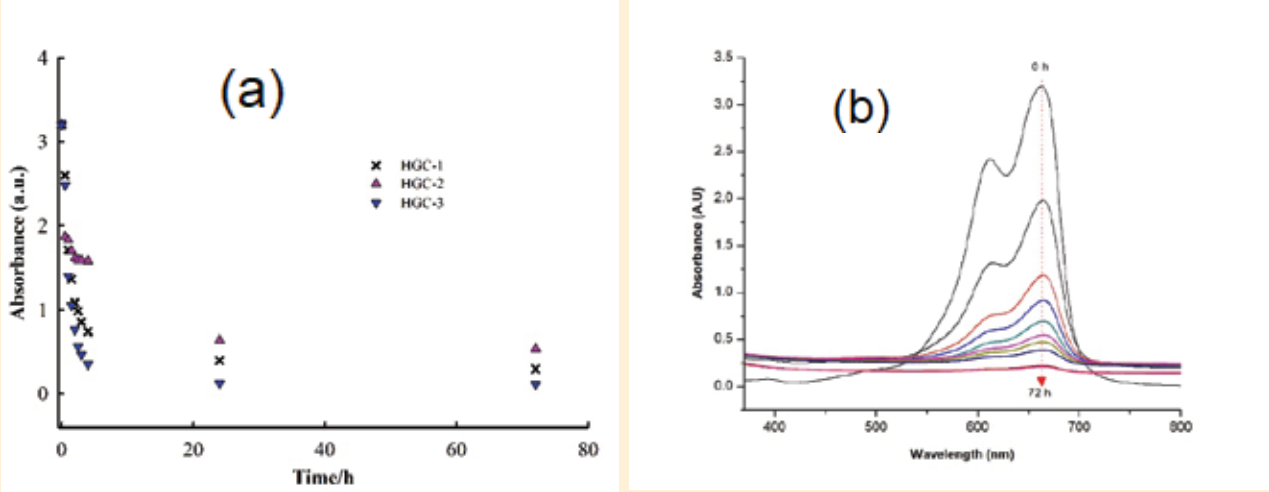

Fig. IV(a). Variation of absorbance with time for adsorption of MB on HGC-1, HGC-2 and HGC-3 respectively. (b) Adsorption spectrum of methylene blue on HGC-3.

The absorbance-time profiles of adsorption of MB on HGC-1, HGC-2 and HGC-3, respectively have shown in Figure-4(b). It can be seen that absorbance of the solution decreases with time up to 120 min and then become constant. This time (120 min) is considered as the equilibrium time for the adsorption of MB. However, in the case of HGC-3, the extent of decrease in absorbance is larger than that of HGC-1 and HGC-2.

However, from the measured absorbance, the amounts of MB adsorbed on HGC-1, HGC-2 and HGC-3 per gram were estimated and are demonstrated in Figure-4(a). In all cases, the progress of MB adsorption was fast, and HGC was nearly saturated within 120 min. The extent of adsorption seems to be different for different HGCs. The cationic dye, MB showed significant adsorption on HGC-3 having more molar ration of MA compared to HGC-1 and HGC-2. However, at equilibrium condition, the amounts of MB adsorbed on HGC-1, HGC-2 and HGC-3 are found to be 0.455, 0.336 and 0.524 mg/g, respectively. All the composites strongly adsorbed a significant amount of MB. But HGC-3 adsorbed MB is about 15 % and 56 % higher than those on HGC-1 and HGC-2, respectively. Therefore, HGC-3 composite shows highest adsorbent capacity.

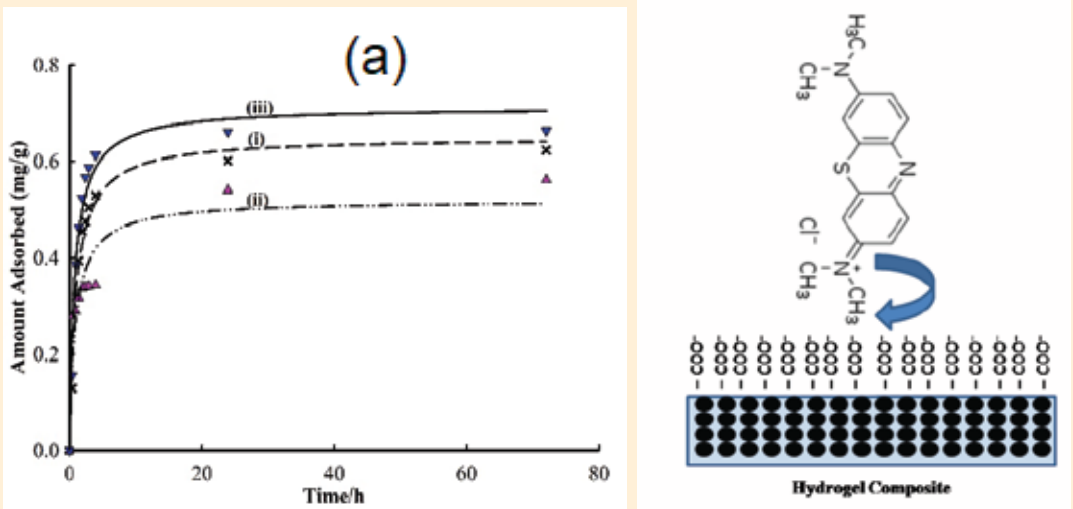

Fig. V.(a). Adsorption of MB on (i) HGC-1, (ii) HGC-2 and (iii) HGC-3 in aqueous solution. (b) Probable interaction site between MB and hydrogel composite.

Proposed mechanism of MB adsorption on HGC

MB is a cationic dye containing positive charge on the $-N(CH_3)_2$ groups. HGC prepared from PVA, HPMC and MA contains negative charge of the structure become electron rich. So, mode of adsorption of MB on HGC is the electrostatic interaction between positively charged MB and negatively charged HGC (Figure-5(b)). As a result, MB are readily adsorbed on HGC surfaces. However, the adsorbed amount of MB is maximum on HGC-3. This may be due to presence of more percentage of MA in the HGC composition which contains negatively charge on carboxylate ions.

Drug release study

Fig. VI. UV-visible spectrum of (a) paracetamol solution (b) paracetamol loaded HGC solution

Figure-6 represents the drug release profile of prepared HGCs. From the graph it is shown that no drug was released from the composites after 0.5, 1.0, 2.0 h intervals. No change i.e., no peak of paracetamol was found. Then, the release medium was kept at room temperature for 24 h and UV-spectrum of the release medium was taken for each HGC and again no peak was observed which indicates that the drug was strongly adsorbed onto HGCs. This may be due the strong electrostatic interaction of free –OH group in the structure of paracetamol and carboxylic group in the HGCs.

Conclusion

In this study, maleic acid was successfully cross-linked with PVA and HPMC. The cross-linked macromolecular support was characterized by FTIR spectroscopy. FTIR spectrum of the prepared HGC materials clearly indicated the formation ester group. TGA spectrum shown the variation of thermal stability with varying the amount of cross-linker. UV-visible spectrum of evidenced the adsorption of dye methylene blue onto the HGC materials. Furthermore, HGC materials were used to include paracetamol drug. Complete adsorption of paracetamol onto the HGC materials was confirmed from UV-visible spectrum.

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