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Morphological Effect on Swelling Behaviour of pH– Sensitive Hydrogels

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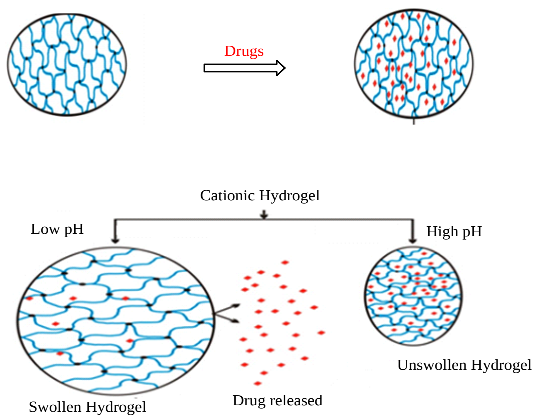
Abstract
Hydrogels are three-dimensional hydrophilic polymeric network, that are capable of holding or intake large amount of water or biological fluids. In this study, attention is paid to synthesis a pH-sensitive biopolymeric hydrogel from heterocyclic compound. The surface morphology of the synthesised biopolymeric hydrogel was investigated using Scanning electron microscopic (SEM) analysis. Swelling studies of hydrogels at various pH media ranging from 3.0 to 10.0 were also investigated. This study reveals interaction between solvent and hydrogel network. The rough surface excavation morphology of hydrogel affects the swelling behaviour. Greater water imbibing tendency of hydrogel with smart pH-sensitivity may be considered an excellent candidate for industrial, environment and biological applications.

GRAPHICAL ABSTRACT



Keywords
Biopolymeric hydrogel, pH sensitive, Hetero cyclic compound, swelling equilibrium etc...

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INTROTUCTION

Hydrogels have been a topic of extensive research in the past decades due to their properties such as, their high water content and the possible control over the swelling kinetics make them very attractive for biomedical applications[1-4].Hydrogels are composed of hydrophilic homopolymer or copolymer network and can swell in the presence of water or physiological fluids. The water Hydrogels are materials that display three-dimensional network of hydrophilic polymers, which are able to absorb and keep a large amount of water within its network[5]. Hydrogels are three-dimensional networks which are formed by copolymerization of monomers with or without cross linking agents. These gels are capable to absorb vast amounts of water because of their hydrophilic features [6,7] holding capacity of the hydrogels take place mainly due to the presence of hydrophilic groups, viz. amino, carboxyl and hydroxyl groups, in the polymer network [8,9].

Hydrogels are sensitive to specific environmental changes and show responses by changing their shape or volume when exposed to definite conditions are referred as stimuli sensitive hydrogels. These are sensitive to (a) physical stimuli such as light, pressure, temperature, (b) chemical stimuli such as pH, ionic strength, and (c) biological stimuli such as enzymes, antigens. Amongst the stimuli responsive hydrogels, pH sensitive hydrogels are the most studied hydrogels. The key factors for controlling the properties of pH sensitive hydrogels are ionic charge, pKa or pKb values of ionizable groups, degree of ionization, hydrophilicity, polymer concentration, and pH of the swelling medium.

The pH sensitive hydrogels containing pendant acidic or basic groups such as carboxylic acids, sulfonic acids, primary amines, or ammonium salts which change ionization in response to change in the pH have become the subject matter of major interest for use as carriers in drug delivery research. The natural pH of the gastrointestinal region of the human body varies from acidic in the stomach to neutral in the intestine. [10,11]. Cationic hydrogels like polyethylene, swell at acidic medium (low pH) due to protonation of amino/imine groups. The protonated positively charged moieties on the polymer network cause repulsion which weaken the bond i.e stability decreased and hence fluids are entered which responsible for swelling. These types of hydrogels can be used for drug (antibiotic) delivery to the stomach during ulceritis or as carriers for an injectable drug delivery system [12,13].

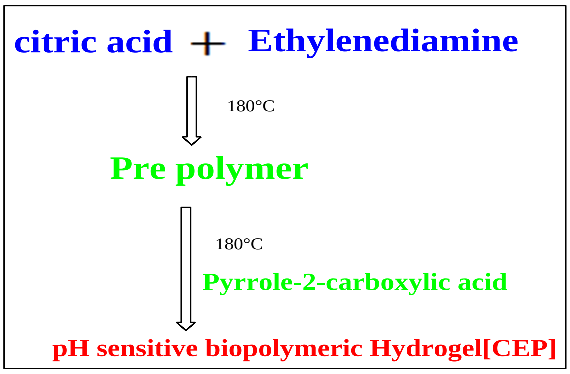
Previously our group reported the pH sensitive hydrogel based on renewable resource-based monomer and Indole-3 Acetic Acid (IAA) to focus on pH sensitivity with very attractive biomedical applications [14-19]. The present work aimed at the preparation of new swelling behaviour of pH sensitive biopolymer materials having potential durg to obtain stimuli-responsive hydrogels in times that are shorter and by using protocols that are easier than those typically used and reported so far. Namely citiic acid, Ethylenediamine and Pyrrole-2-carboxylic acid-based hydrogels and characterized and compared in terms of their swelling behaviour in various pH media and morphology by SEM analysis.

EXPERIMENTS

MATERIALS AND METHODS

Anhydrous citric acid (CA), Ethylenediamine (EDA) and Pyrrole-2-carboxylic acid (PCA) were purchased from Sigma-Aldrich (Chennai, India). Ethanol was purchased from Merck (India). Demineralized water used throughout the process.

PREPARATION OF PH SENSITIVE BIOPOLYMERIC HYDROGEL



FOURIER TRANSFORM INFRARED SPECTRAL STUDIES

FT-IR spectra of hydrogels were recorded by using Shimadzu spectrophotometer-8400S (Japan) in KBr medium at room temperature in the region of 4000-400 cm-1.

SWELLING EQUILIBRIUM STUDIES

Dried hydrogels were allowed to hydrate in buffer solutions with different pH values for 48 hours in the various pH from 3.0 to 10.0. After being fully hydrated, the samples were taken out and the excess water on their surface was gently removed by filter paper. The weights of the hydrating samples were measured at timed intervals. The swelling equilibrium % was calculated by the following equations,

$$S_{eq}\% = \frac{W_{eq} - W_d}{W_d} \times 100 \rightarrow \quad (1)$$

Where,

W_{eq} - Weight of gel at equilibrium

W_d - Weight of dry gel

SCANNING ELECTRON MICROSCOPY

Micro structure characterization of hydrogel was conducted by Hitachi, Model: S-3400 scanning electron microscopes. A remarkable three-dimensional appearance with high resolution was obtained in the polymer hydrogels. All the samples were freeze dried and kept in vacuum for silver sputtering treatment before scanning.

RESULTS AND DISCUSSION

FOURIER TRANSFORM INFRARED SPECTROSCOPY

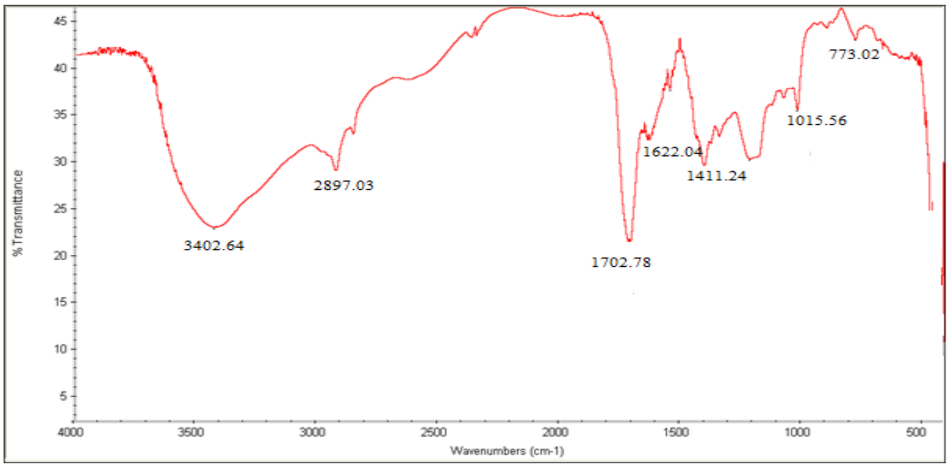


Fig: 1 FTIR spectra of CEP hydrogel

The FTIR spectra of synthesised hydrogel have shown in **Fig. 1**. FTIR spectroscopy clearly gives idea about cross-linking and conjuction of citric acid into the polymer (i.e., CA conjucated with EDA and PCA). FTIR of cross linked CA with EDA was shown in peak at 3402 cm-1, may be due to –NH stretching of free amino group in EDA and peak at 1622cm-1 may be of free stretching of amide bond that is formed between EDA cross-linked with CA and PCA, which indicates EDA conjucated in polymer.

Fig.1 in which the absorption band at 2897cm-1 due to asymmetric -CH - stretching of CA. In addition to that , the peak at 1411cm-1 may be due to -C=C- aromatic stretching of pyrrole ring and also it reveals that, the presence of pyrrole ring in the polymer network It shows peaks at 1702cm -1 which may be due to the presence of free –COOH groups of CA in the prepared polymer. The broad peak at 3402cm-1 cab be attributed to the hydrogen bonded –OH in CA or –NH bond or both overlapped [20,21]. An absorption at 1622 cm^{-1} due to bending vibration of –NH bond in CEP [14]. The peak at 1702 cm^{-1} due to the presence of secondary amine by the condensation of citric acid and Ethylenediamine. These results confirmed there was no change in –NH group in PCA. An absorption around 1015cm-1 due the presence of –CH of pyrrole [22].

SWELLING STUDIES OF CEP HYDROGEL:

The swelling studies of hydrogels were measured for hydrogels by varying pH ranges between 3.0 and 10.0, at ambient temperature (25 °C). The hydrogel sample were immersed in various pH buffer solutions for at least 24hours. Incorporation of Pyrrole-2-carboxylic acid composition found to have altered the swelling behaviour. This might be due to the electrostatic repulsion among the ionic charges in the polymeric hydrogels. The swelling equilibrium reacts better in the acidic medium compared with basic medium due to the protonated amino group present in the polymeric network, decreasing osmotic pressure and electrostatic repulsion [22].

In table 2 it shows that swelling was maximum at low pH than higher pH for CEP.

S.No.	Sample Code	pH					
		3	4	6	7	9	10
1	CEP	1500	1400	1350	1250	1050	900

The CEP biopolymeric hydrogels showed pH dependences. The equilibrium swelling found to be higher at acidic (low pH) than alkaline (high pH). The Seq% values are 1500, 1400, 1350, 1250, 1050 & 900% at pH 3, 4, 6, 7, 9 &10 respectively. The protonation of amino groups grades in the high osmotic pressure and electrostatic repulsion between protonated amino groups (–NH) of polymer chains, which leads higher swelling of hydrogel in low pH. But on the other side at high pH dwindling of osmotic pressure and electronic repulsion take place which leads to decrease in swelling nature [23,24].

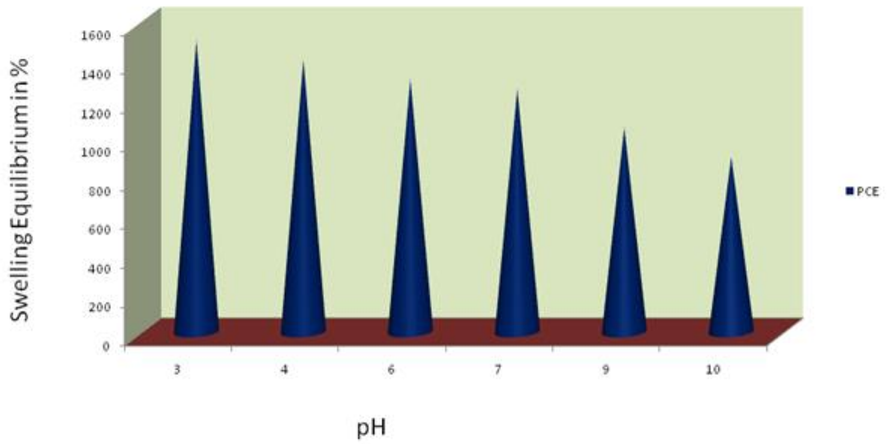


Fig: 2 Swelling equilibrium of CEP hydrogel

SEM MORPHOLOGIES OF BIOPOLYMERIC HYDROGELS

SEM analysis is a superior network used to study the morphological changes of CEP hydrogels. At 10,000×1µm (Fig. 3a) and 30,000×0.5µm (Fig. 3b) magnification, the porous surface structure of the CEP hydrogel was shown. These porous or cavities has been used to enhance the absorption of fluids more effectively. SEM analysis of CEP hydrogels shows an uneven and coarse surface, which can be beneficial to the swelling properties in different pH solutions [25], which is convenient for the penetration of water into the biopolymeric 3-D hydrophilic network. This porosity property of hydrogels helps in the release of drugs from hydrogels. The SEM results well supported the results of swelling equilibrium.

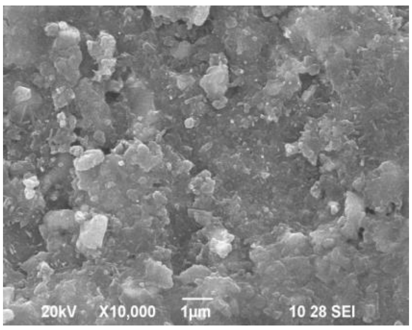


Fig: 3a

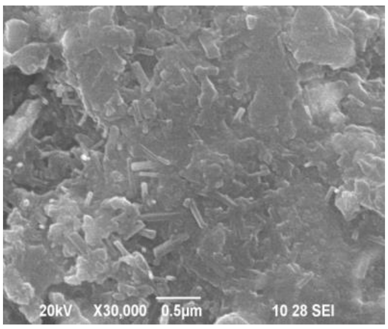


Fig: 3b

Fig: (3a&3b) SEM IMAGES OF CEP HYDROGEL

CONCLUSION

In the present investigation, pyrrole-2-carboxylic acid-based hydrogels were synthesized via condensation polymerization using citric acid, ethylenediamine and pyrrole-2-carboxylic acid. A green synthesis method was adopted for the preparation hydrogels. The process adopted was environment-friendly,free from toxic chemicals was successfully utilized to synthesize CEP hydrogels. The formation of CEP biopolymeric hydrogels have been confirmed by FT-IR spectroscopic analysis. The porous surface morphology of hydrogels has been confirmed by SEM analysis. This SEM analysis supported swelling nature of hydrogels. The swelling equilibrium percentage was found at various pH 3-10 revealed higher swelling in acidic medium than basic medium. The results of all studies imply that, Synthesised hydrogels may be recommended for eco-friendly, toxic less biomedical applications such as controlled release of drugs to pH sensitive parts of human being.

CONFLICT OF INTEREST

The authors don't have any conflict of interest.

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