

Carboxymethyl Cellulose-Starch-Gelatin Based Hydrogel Membranes for Heavy Metal Removal

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Abstract:- Water pollution is one of the most prevalent problems affecting people throughout the world, while adsorption is the most widely used method to remove the contaminants from water. In this present study, a series of eco-friendly Sodium salt of carboxymethyl cellulose-Starch-Gelatin hydrogels were prepared using Citric acid as the chemical crosslinker by changing biopolymers and crosslinker percentages. Characteristics of the hydrogels were investigated by swelling test and Fourier Transform Infrared (FTIR). Swelling behavior was tested in cold and hot water, acids, alkalies salt water etc. Water uptake by the hydrogel increased when starch concentration increased but decreased when gelatin and crosslinker concentration increased. Further, the hydrogel was evaluated as a bio adsorbent for the removal of dyes, namely Crystal violet and Rhodamine B from water. Maximum dye adsorption was seen for crystal violet. Metal adsorption was also studied using copper sulphate solution.

Keywords:- Membranes, Hydrogels, Dye Adsorption, Cellulose Etc.

I. INTRODUCTION

Hydrogels are polymer networks possessing the ability to absorb water-based fluids, swelling to form a hydrated interlinked network [1] (Sharma, R. et;al, 2015). Wichterle and Lim synthesized the first synthetic hydrogel in 1954 for the manufacturing of contact lenses (Weerasundara, L et;al 2020)[2]. Hydrogels have three dimensional structures which is due to the presence of crosslinks between the polymer chains. Crosslinking between polymer chains can be due to (a) Physical crosslinking (b) Chemical crosslinking (Khan, S et;al. 2016)[3]. Electrostatic interaction, Coordination bonds, Hydrophobic interaction and Hydrogen bonding are responsible for the formation of physically crosslinked hydrogels. These hydrogels have a sol-gel phase transition when exposed to external stimuli. On the other hand, chemically crosslinked hydrogels have ionic or covalent bonds between the polymeric chains. In chemically crosslinked hydrogels there is a volume phase transition when it is exposed to external conditions like temperature, pH, ionic strength and electric field (Thakur, S. et;al. 2017)[4].

Hydrogels have the ability to absorb huge quantity of water. It can absorb water, about 10-20 times more as compared to their original molecular weight. The swelling capacity of hydrogels depend on the porosity of the network. Porosity of hydrogels depend on (a) attraction between hydrogels and aqueous solution (b) cross linking density. The porosity can be permanently achieved by doing various modifications like integrating nanoparticles, cryogelation, crosslinking polymerization and grafting mechanism (Thakur, S et;al. 2018)[5].

Environment is highly affected by the water pollution from various industrial effluents of dyes, heavy metal ions, and other organic contaminants such as pesticides, drugs, etc[6]. Water quality of the waste from the dye industry contributes enormously and makes it unfit for drinking. There is a severe scarcity of water and thus drinking water to be protected and the scientific and general community should contribute greatly. There are various methods available like membrane filtration, coagulation, ozone treatment, photocatalytic degradation, ion exchange, biological treatment. These methods are used for the removal dyes from wastewater. Adsorption is an easy, practical, and cost-effective method [7]. To absorb dyes materials with high adsorbing quality is required. Hydrogels are with three-dimensional structures hydrophilic in nature can have greater water retention. Natural polysaccharides, starch, gelatin, chitosan, sodium alginate, gums, polypeptides, agar are polymeric hydrogels. Out of which carboxymethyl cellulose (CMC) widely used due to their wide range of applications. These materials are used in the fields of biomedical, pharmacy, nanotechnology, electrochemical capacitor, and water and soil treatment [8]. Dye industry gives out Rhodamine B (RhB), Methyl orange (MO), and Methyl violet (MV), into water bodies without any treatment are hazardous have adverse effects on the environment and the ecosystem. These materials are carcinogenic and mutagenic, and high concentrations can cause hypertension, fever, confusion, staining of skin and decoloration of urine [9]. Conventional polysaccharide hydrogels are renewable, biodegradable, eco-friendly and non-toxic in nature. Limitations are low thermal and mechanical properties which make it's usefulness in applications like tissue engineering, adsorbent, drug delivery. The design of stable polymeric hydrogels with the network structure giving crosslinking is of greater scope. Reactive functionalities present on polymeric and thus network structure in different polymers using various

chemical and physical cross-linkages is possible [10,11]. CMC is crosslinked to form a three-dimensional polymeric hydrophilic network, and can absorb large amount of water [12,13]. Gel strength can be increased with Gelatin, an ionic hydrophilic linear polypeptide with the –NH₂ and –COOH functionalities also, hydrophilicity and functional properties of the hydrogels [14-17].

The current work proposes the making of hydrogel based membranes for the adsorption of dyes present in waste water. Controlled crosslinks are to be given for the swelling and adsorption of dyes.

Experimental

Materials and physical measurements CMC sodium salt (degree of substitution (DS) = 0.7, average molar mass (Mw) = 250 kDa and viscosity 250–350 cps for 2% solution at 20 °C), gelatin (gel strength: 225 g Bloom, type B from bovine skin), sodium periodate, sodium hydroxide, ethanol, copper sulphate, Rhodamine-B (RhB), crystal violet were obtained from Loba Chemie. All reagents used were of analytical grade and solutions were prepared using distilled water.

Preparation of hydrogels: Sodium salt of carboxymethyl cellulose (CMC), starch and gelatin were used to prepare hydrogels as per the formulations given in Table 1. Different sets of hydrogels were prepared by varying the concentration of biopolymers. Citric acid was used as the cross-linking agent.

Sodium salt of Carboxymethyl cellulose powder was dissolved in distilled water, and it was homogeneously mixed using a magnetic stirrer for 2 hours at 60°C. Similarly, starch was mixed in distilled water for one and half hour. Gelatin was dissolved in distilled water. Citric acid was prepared by dissolving the specified amount in distilled water. Then the three solutions were mixed together and citric acid (cross-linking agent) was added to the solution. The solution was mixed continuously at 60°C for 3 hours on a magnetic stirrer. Later the solution was poured into a petri plate and air dried for two days. The amounts of the components used to form hydrogels are listed in the table given below:

Table 1: Formulations

HYDROGEL SET	Na-CM C (%)	GELATIN (%)	STARCH (%)	CITRIC ACID (%)
SET 1	100	10	10	2
SET 2	100	10	20	2
SET 3	100	10	30	2
SET 4	100	10	40	2
SET 5	100	20	10	2
SET 6	100	30	10	2
SET 7	100	40	10	2
SET 8	100	20	10	3
SET 9	100	20	10	4
SET 10	100	20	10	5

Physical Property Analysis: The percentage yield of hydrogels was calculated and the thickness of the hydrogel film was determined using a thickness gauge.

Retention analysis:

The water absorption ability of the prepared hydrogels in room temperature was tested by dipping the hydrogels in water at room temperature for 2 hours. Tea bag method was used to find the water absorption of the gels. Similarly, the water absorption was checked in hot water. The hydrogels were immersed in hot water (60°C) for two hours. The amount of water absorbed was calculated by subtracting dry weight from wet weight of hydrogel. Test was carried out in triplicates. Tea bag method used to check the water uptake in room temperature and at 60°C respectively.

Water swelling: The swelling behavior of the hydrogels in normal water and hot water were studied. The hydrogel swells in an aqueous medium due to absorption of water due to various van der Waals interactions among water and the different hydrophilic functional groups present on the hydrogel backbone. The swelling of a hydrogel is a result of diffusion of water into polymeric hydrogel network which causes expansion of polymeric network (Sethi, S et.al 2020)[18]

The hydrogels were dipped in 0.1 N HCl for two hours. Tea bag method was used to carry out the test. Similarly, alkali resistance was determined by immersing the tea bag in 0.1 N NaOH. Test was carried out in triplicates. The water absorption was calculated by subtracting dry weight from wet weight of hydrogel.

The hydrogels were oven dried for two hours at 60°C. The initial and final weight was measured for further calculation. Heat ageing of hydrogels was calculated by subtracting final weight from initial weight of the hydrogel. The absorption of salt water by these hydrogels were tested by dipping the hydrogel in salt water. Three types of salt concentration were taken (2%, 4% and 6%) for the work. 5g, 10g and 15g for Sodium chloride was dissolved in 250 mL distilled water to make 2%, 4% and 6% solution respectively. Tea bags containing hydrogels were dipped in each solution for two hours. The weight of the dry and wet hydrogels was measured. Amount of water uptake was calculated by subtracting dry weight from wet weight of hydrogel. The amount of salt absorbed by the hydrogels was determined separately for each hydrogel. 2% Sodium chloride solution was prepared by dissolving 1g NaCl in 50 mL distilled water. 0.1g of hydrogel was taken for the test. The hydrogels were immersed in salt water for four hours. Later the hydrogels were removed from the solution and the salt solution was poured into a Petri plate. The solution was air dried for three days and the amount of salt present in the petri plate was weighed using weighing machine. The amount of salt absorbed by the hydrogels was calculated by subtracting the final weight of salt obtained after evaporation from the initial weight of NaCl taken at the beginning.

FTIR (Fourier transform infra-red) spectroscopy: Set 5, 6 and 8 Hydrogels were characterized by FTIR spectroscopy in the range of $4000\text{-}350\text{cm}^{-1}$ at room temperature. An FTIR spectrophotometer (M/s. Perkin Elmer, spectrum two) was used for the study.

Dye absorption : The treatment and removal of dyes from waste water is one of the challenges faced by the environmentalists and industries. Low-cost biopolymer-based hydrogels with high adsorption capacity, biodegradability and biocompatibility can be considered as good candidates for adsorption of dyes from wastewater. In the present study, Set 5, Set 6 and Set 8 hydrogels were utilized as an absorbent for the removal of Copper sulphate, Crystal violet and Rhodamine B. Dye absorption was carried out using UV- visible spectrophotometer.

Absorption studies: 1% copper sulphate solution was prepared by dissolving 1g copper sulphate in 100 mL distilled water. 0.1g hydrogel sample was taken for the test. The three hydrogels were dipped into 1% copper sulphate solution separately. The wavelength of maximum absorption of copper sulphate was determined. The absorbance value of the solution containing the hydrogel was determined at every 0hr, 2hr, 4hr, 6hr and 24hrs. Experiment was repeated for Crystal violet and Rhodamine B

Desorption study: The reusability of hydrogel after dye absorption was investigated by immersing the used hydrogels in 0.2 N HCl for 24 hours.

II. RESULTS AND DISCUSSION

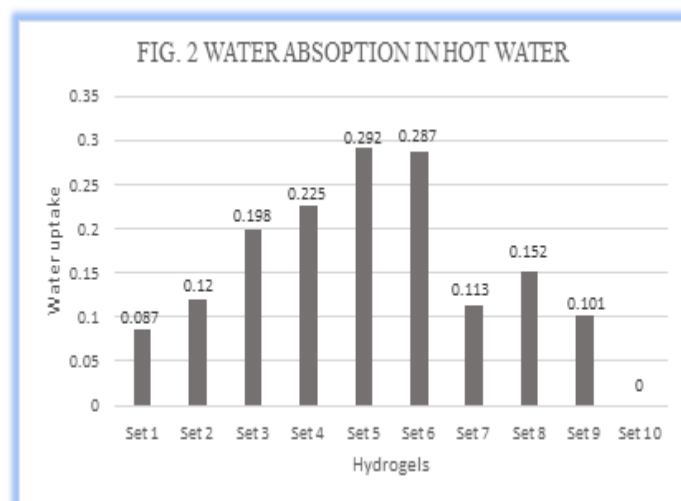
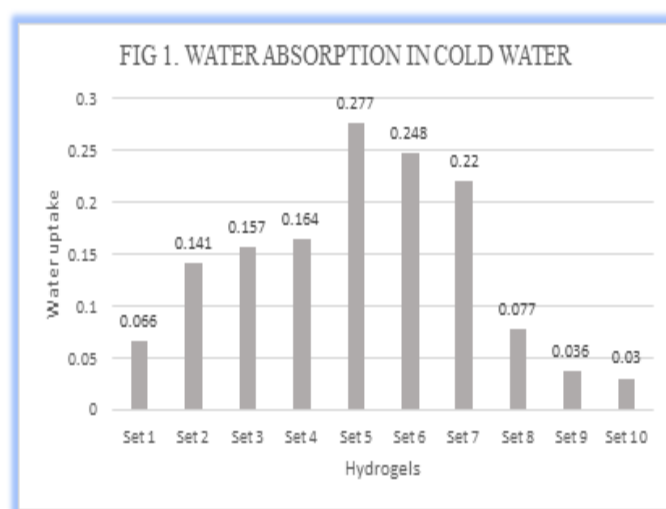
Table 2: Physical Properties

HYDROGELS	PERCENTAGE YIELD (%)	THICKNESS (mm)
Set 1	89.78	0.23
Set 2	69.93	0.20
Set 3	70.25	0.175
Set 4	86.05	0.171
Set 5	88.53	0.079
Set 6	88.45	0.178
Set 7	89.70	0.085
Set 8	74.56	0.208
Set 9	79.28	0.287
Set 10	84.73	0.369

The water uptake capacity of each hydrogel in cold water is given in Fig:1. The water uptake capacity of each hydrogel in hot water is given in Fig:2 Maximum water uptake is seen in set 5. In set 1-4 the water uptake by the hydrogels in both cold and hot water have been showing an increasing trend. This is due to the increase in starch concentration. As the concentration of starch increases the water absorption capacity also increases. In set 5-7 the water absorption capacity in both cold and hot water have been showing a decreasing trend. This is due to the increase in the presence of higher levels of triple helix in gelatin. As the triple helix content of gelatin increases, the strength of the hydrogel increases and this results in the decrease in the swelling property of the hydrogel (Pal, K et.al. 2007)[19]. The effect of crosslinker concentration on swelling capacity

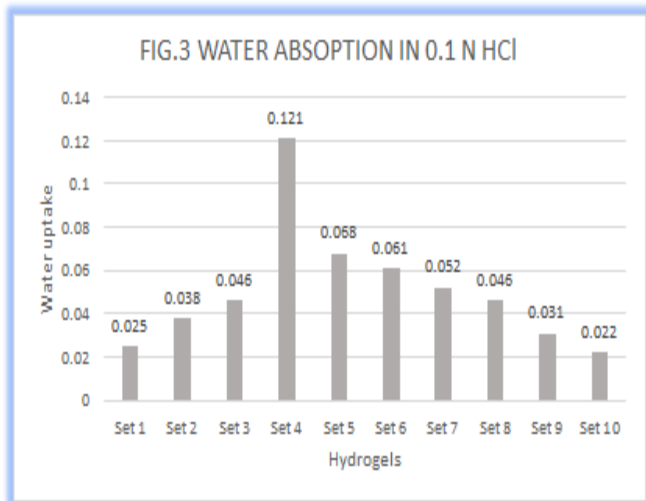
of the hydrogels was investigated. As shown in Figure, in Set 8 -10 the swelling property of the hydrogels in both cold and hot water is showing a decreasing trend. This decrease is due to the increase in the crosslinker concentration. As the crosslinker concentration increases the free space between the copolymer chains decreases which results in highly rigid structure (i.e., the network chains become inflexible) which cannot expand much to hold a large quantity of water (Pourjavadi, A et.al 2007)[20].

As shown in Fig 1 the water uptake capacity of the hydrogels at higher temperature is more than the water absorption at room temperature. This might be due to the enhanced thermal mobility of polymer chains and decrease in the crosslinked density of the hydrogel with increasing temperature (Sethi, S et.al 2020[18]).



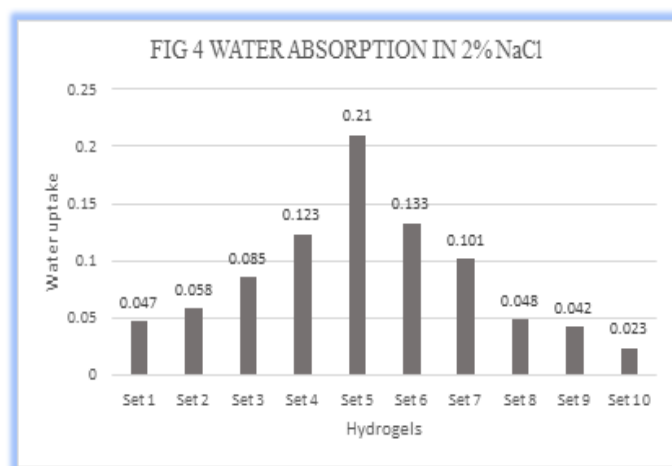
Swelling behaviour in 0.1 n hydrochloric acid :The water uptake capacity of the hydrogels was tested in 0.1N HCl. The hydrogels were found to be acid resistant. The water uptake capacity of the hydrogels in 0.1N HCl is less as compared to the water uptake capacity at room temperature. CMC is a polyelectrolyte, which shows sensitivity to pH and ionic strength variations. The pKa of carboxylic acid groups contained in the polymer is about

4.5. At acidic pH, most of the –COOH groups on Na-CMC backbone remain protonated, resulting in lower water absorbency. At pH values ranging from 4.0 to 6.0, –COOH and –NH₂ groups mostly remain neutral or unchanged, thereby decreasing repulsions and consequently increase in the swelling property (Sethi, S et.al 2020)[18].



Swelling behaviour in 0.1 N Sodium hydroxide: The water uptake capacity of the hydrogels in 0.1N NaOH was tested. All the 10 sets of hydrogels got completely dissolved in 0.1N NaOH solution. This shows that the hydrogels are not alkali resistant. The reason behind the hydrogels getting dissolved can be due to breaking of hydrogen bonds, electrostatic repulsion between macromolecules and higher rate of water uptake. Since the pKa of the carboxylic acid in the polysaccharide is 4.5, at higher pH the carboxylic acid groups become deprotonated. And the hydrogen bonds would be broken between the molecules and the hydrogel gets dissolved in NaOH solution (Barbucci, R et.al; 2000)[19].

Swelling behaviour in sodium chloride solution: The swelling behavior of the hydrogels were tested in three different concentration of sodium chloride solution (Figure 4). The water absorption was tested using 2%, 4% and 6% sodium chloride solution. The hydrogel set 5 showed the maximum water uptake in all the three concentrations. The water uptake in salt solution is lesser than the amount of water uptake in distilled water. The swelling capacity of hydrogel is significantly affected by various factors of the external solution. For instance, swelling ability of ‘anionic’ hydrogels in various salt solutions is less as compared to the swelling values in distilled water. This undesired swelling-loss is often attributed to a ‘charge screening effect’ of the additional cations causing a non-perfect anion–anion electrostatic repulsion. The cations in the salt solutions screen the polar groups causing reduction in the hydrogen bonding with H₂O molecules. Because of which, the osmotic pressure resulting from the mobile ion concentration difference between the gel and aqueous phase decrease and consequently the absorption rate decrease (Pourjavadi, A et.al 2007)[20].



Salt absorption: The amount of salt uptake by the hydrogels of set 1-7 was tested by dipping the hydrogels in 2% NaCl solution for 4 hours (Figure 5). Only a small amount of salt was absorbed by hydrogels of set 4, 5 & 6. Among the three sets of hydrogels, set 5 showed maximum uptake. Other hydrogels didn’t show any salt uptake.

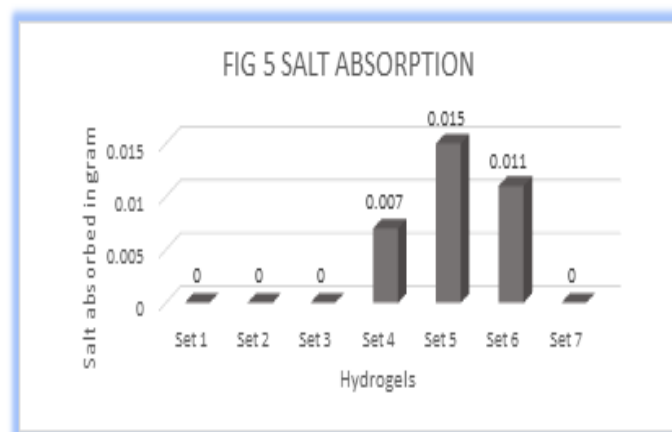


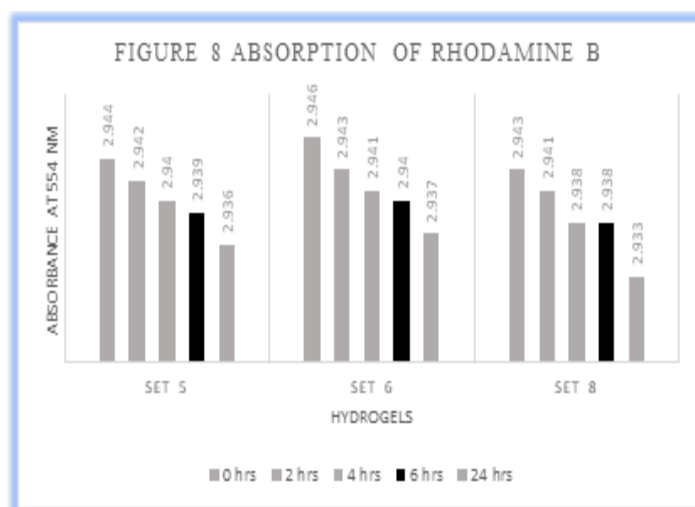
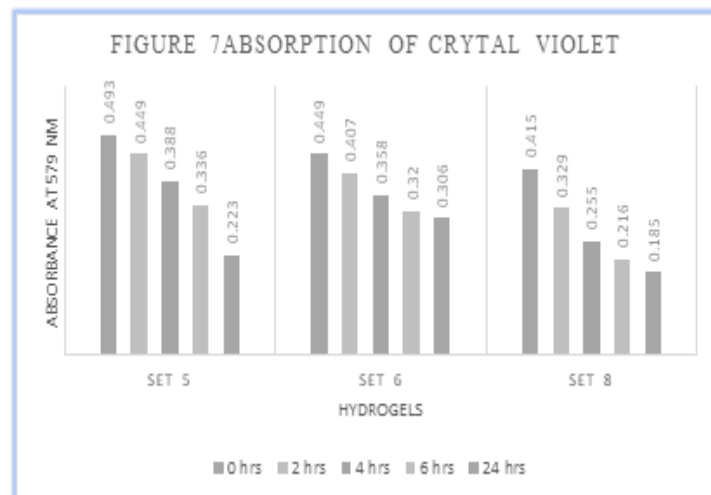
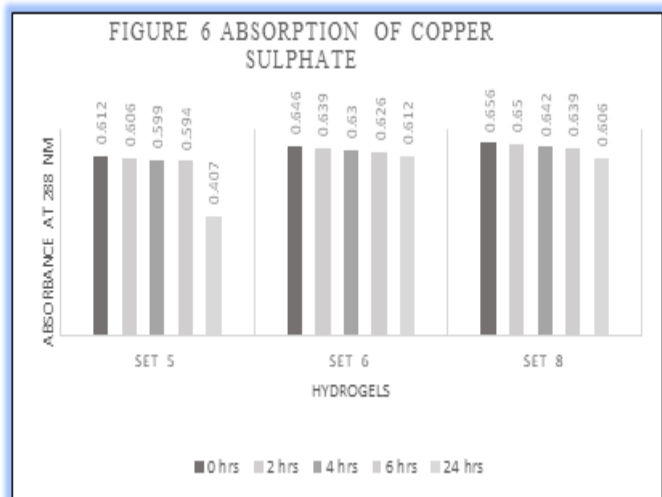
Fig 21: Amount of salt absorbed by hydrogels

Heat ageing: Heat ageing of the hydrogels was tested by oven drying the hydrogels at 60°C for two hours (Table 3). Table shows the weight loss of the hydrogels on oven drying. The weight loss observed for the hydrogels is due to loss of water molecules present in the hydrogel films as water vapour. The hydrogels were not damaged or degraded when kept at 60°C.

Table 3. Heat ageing effects as weight change

HYDROGELS	HEAT AGEING, weight change gms
Set 1	0.004
Set 2	0.004
Set 3	0.003
Set 4	0.003
Set 5	0.004
Set 6	0.002
Set 7	0.002
Set 8	0.003
Set 9	0.004
Set 10	0.002

Dye absorption studies : Figure 6,7 and 8 are showing the absorption studies of hydrogels with copper sulphate, crystal violet and Rhodamine dyes in contact with the hydrogels respectively. UV absorption values are plotted along the y axis and time in hours in x axis. The results show that the hydrogels are absorbing the dyes and the UV absorption peak is getting reduced as time proceeds. Rhodamine and crystal violet give better absorption compared to copper sulphate with the hydrogel formulations. The sets show more crosslinking as per the numbers. The crosslinks can make the absorption stable and thus shows higher absorption values.



1% Copper sulphate solution was used to test the adsorption rate of the three sets of hydrogels (i.e., Set 5, 6 and 8). The λ_{max} of copper sulphate solution was found to be at 288nm. The dye adsorption by the hydrogels were determined at various time intervals. Figure 6 shows the adsorption rate of the three hydrogels. From the results we can say that the hydrogels adsorbed copper sulphate from the solution. From this result it can be said that the hydrogels can be used for the removal copper sulphate from water. Maximum adsorption of copper sulphate was seen in Set 5 followed by Set 8 then Set 6.

0.004% Crystal violet solution (cationic dye) (Figure 7) was used to test the adsorption rate of the three sets of hydrogels (i.e., Set 5, 6 and 8). The λ_{max} of crystal violet solution was found to be at 579nm. From the results we can say that the hydrogels adsorbed crystal violet from the solution. From this result it can be said that the hydrogels can be used for the removal crystal violet from water. Maximum adsorption of crystal violet was seen in Set 5 followed by Set 8 then Set 6. 0.004% Rhodamine B solution (cationic dye) (Figure 8) was used to test the adsorption rate of the three sets of hydrogels (i.e., Set 5, 6 and 8). The λ_{max} of Rhodamine B solution was found to be at 554nm. From the results we can say that the hydrogels adsorbed Rhodamine B from the solution. From this result it can be said that the hydrogels can be used for the removal Rhodamine B from water. Maximum adsorption of Rhodamine B was seen in Set 8 followed by Set 5 then Set 6.

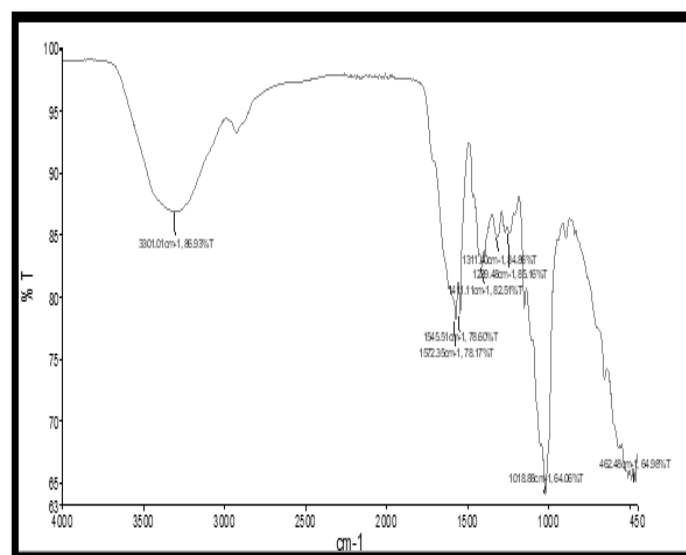


Figure 9 FTIR of Set 5

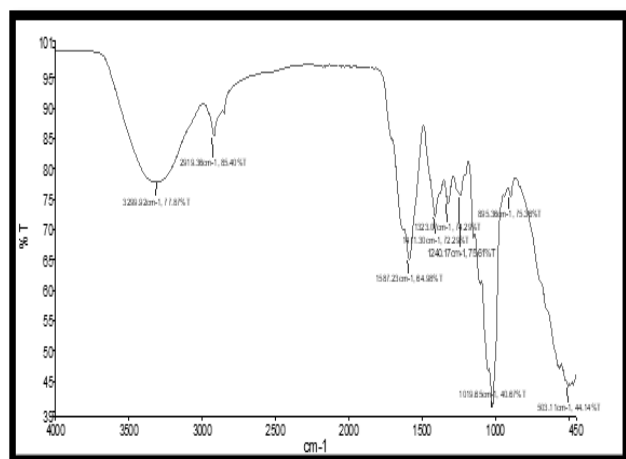


Figure 10 FTIR set 6

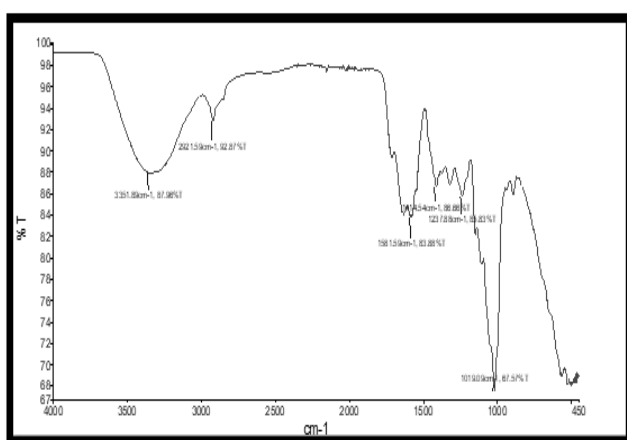


Figure 11 FTIR of set 8

Spectroscopic characterization: Fourier transform infrared (FTIR) spectroscopy was used for identification of the hydrogels. The FTIR spectra of all three samples (i.e, Set 5, Set 6 and Set 8) were recorded in its solid state as shown in Figures 9,10,11 respectively. The FTIR spectra of set are almost same when compared with each other. The functional group region of the three FTIR spectra given below has two peaks. The FTIR spectrum of Set 5, Set 6 and Set 8 hydrogels showed broad and strong absorption at 3301 cm^{-1} (86.93 %T), 3299 cm^{-1} (77.87 %T) and 3351 cm^{-1} (87.96 %T) respectively for O-H stretching vibration of carboxylic acid. Similarly there is a peak at around $2840\text{--}3000\text{ cm}^{-1}$ of medium appearance of C-H stretching of alkane. The three peaks in the three sets of hydrogels at around $1500\text{--}1600\text{ cm}^{-1}$ indicates the stretching of C=C alkene bond.

III. CONCLUSIONS

The hydrogels (Na- CMC- Starch-Gelatin) were successfully synthesized via crosslinking of Na-CMC, Starch and gelatin using citric acid as the crosslinker. The resultant hydrogels had a large degree of water absorbency. The effect of starch and gelatins amount and citric acid concentration showed that with increasing of starch concentration, the water absorbency of the hydrogel

increased. And with the increase in concentration of gelatin and citric acid, the water absorbency of the hydrogel decreased. The chemical morphology of the synthesized hydrogels was confirmed by FTIR spectroscopy. Further, the hydrogel sample was successfully utilized as a bio adsorbent for Copper sulphate, Crystal violet and Rhodamine B dyes in aqueous solution. Based on the current results, CMC-Starch-Gelatin hydrogels have a great potential as a bio adsorbent for the removal of various dyes and heavy metals from waste water. Total ten hydrogels prepared and three were very effective water absorption properties. These three were tested for dye purification. The three hydrogels were effective in adsorption of dyes. Out of which copper sulphate adsorption were comparatively lower, but crystal violet and rhodamine were given higher level of adsorption.

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