PREPARATION CHARACTERIZATION AND OPTIMIZATION OF CARBOXYMETHYL TAMARIND KERNEL GUM-POLY VINYL ALCOHOL HYDROGEL VIA DATA ENVELOPMENT ANALYSIS

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Submitted by: -

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CERTIFICATE

This is to certify that Mr. Himanshu Katyal has satisfactorily completed the project work entitled "**Preparation, characterization and optimization of carboxymethyl tamarind kernel gum-Poly vinyl alcohol Hydrogel via Data Envelopment Analysis**" in completion of the requisite of the honor of Degree of Master of Technology, Delhi during the academic session 2020-2021. This effort has not been reported or submitted in any other University or Institution for honor of any other degree.

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ABSTRACT

Conventional synthesis process usually involves hit and trial approach which is laborious process that consumes ample resources and time. Hence, it's really important to adopt computer-aided techniques of optimization for selecting the optimum parameters which are used in synthesis of material involved. In my work, a novel optimizing technique was used for precise synthesis of carboxymethyl tamarind kernel gum (CMTKG) - poly vinyl alcohol (PVA) based hydrogel which itself is a novel combination. In this total 16 samples were prepared by varying the input parameters such as concentrations of both polymers, initiator and crosslinker and the products formed were analyzed for optimizing the reaction variables using data envelopment analysis (DEA).

Each sample was considered as decision making unit (DMU) in order to get the efficiency frontier. Data Envelopment Analysis was applied to different DMUs to obtain their relative efficiencies according to which efficient and inefficient DMUs were discriminated. Also, to improve the performance of inefficient DMUs, slack analysis was done for CCR DEA model. Slack of inputs shows how much excess amount is there in each DMU which suggest possible reduction in inputs to improve the efficiency of that DMU. Experimentally swelling studies were also carried out in order to validate the model by matching it with the predicted DMU.

This innovative green technique used for accurate synthesis of CMTKG-PVA hydrogel helped in predicting the optimal parameters using less time, labour and resources.

This thesis entitled **"Preparation, Characterization and Optimization of Carboxymethyl Tamarind Kernel Gum- Poly Vinyl Alcohol based hydrogel via Data Envelopment Analysis"** includes the synthesis of hydrogel, its characterization by FTIR, SEM, TGA, DSC and the use of Data Envelopment Analysis for optimizing the reaction variables used in synthesis including study of swelling kinetics and rheological study of the optimized hydrogel. The whole study is compiled in five chapters, (1) Introduction (2) Literature review (3) Experiment Performed (4) Result and Discussion (5) Conclusion

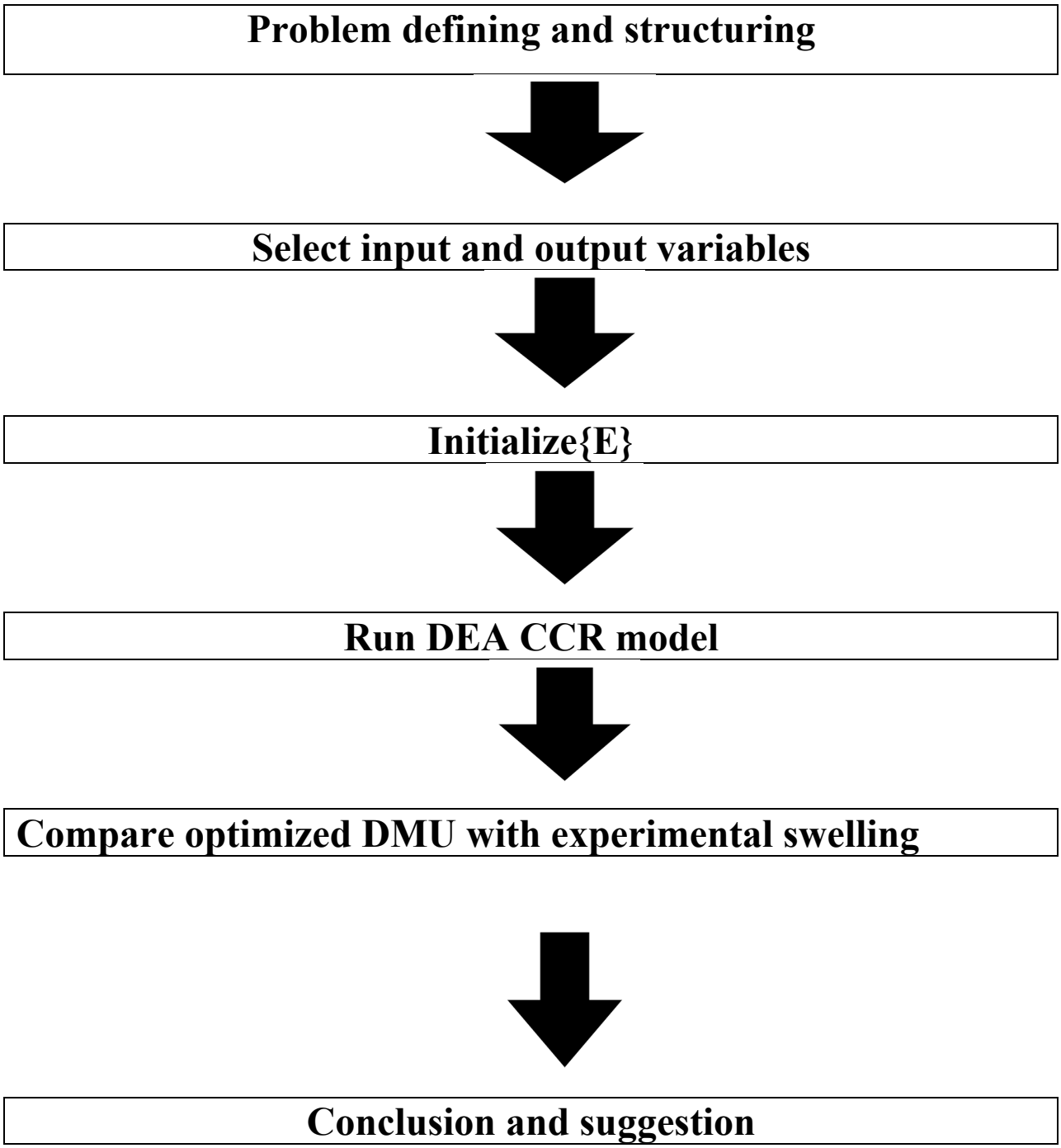

Figure 1: Flow chart showing solution methodology

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Introduction

1.1 Preamble

Hydrogels are 3-D cross-linked hydrophilic polymers that are capable of accumulating and retaining a subsequent amount of water or any other solution plus they have the ability to swell without getting dissolved in it. They are also known as superabsorbent materials which can hold up to hundred times their weight in water [1]. Explanation for the properties displayed by them are due to the hydrophilic functional groups which are joined with the polymeric spine. The hydrogel that can grow upto ninety five percent of their initial dry weight are called superabsorbent hydrogels (SAH) [2,3]. SAH have profoundly thick hydrophilic cation restricting gatherings and contain non fragrant moieties. In general, the hydrogels that are comprised of manufactured polymers are non-biodegradable and even known as toxin or pollutant so this involves worry towards natural contamination. Therefore, the development of natural polymers based or the biopolymers based superabsorbent hydrogel is needed due to its environmental and commercial advantages. Today numerous natural polymers based SAH have been synthesized by utilizing biopolymers in addition to their derivatives like chitosan [4], starch, guar gum and so forth [5,6-9].

Tamarind Kernel Gum (TKG) is a bio polymer and is least expensive gum accessible as it is extracted from the Tamarindus indica L seeds. TKG comprises xylose, galactose and glucose in the molar proportion 1:2:3 [10]. TKG and its derivatives have been utilized as a substitute biopolymer instead of engineered polymers because of its biodegradability, changing solvency, non-poisonous and weakness to microbial degradation [11]. Different TKG based products had been studied till now in different applications including materials, explosives, food, wood and clinical businesses [6]. One derivative of TKG is carboxymethyl tamarind kernel gum (CMTKG). CMTKG has preferred properties over TKG [12]. As per the research gap and to the best of my knowledge CMTKG is being used with PVA. While synthesizing the copolymeric hydrogel, the concentrations of CMTKG, PVA, sodium hydroxide, acrylic acid, potassium persulphate and N,N'-Methylenebisacrylamide were varied and it takes a lot of time in optimizing these reaction variables to get the desired output.

The use of modelling techniques is attracting researchers to fine tune the properties of polymer products and controlling polymerization. The optimization process of chemical reaction variables consumes time and labour, and is tedious often when it is done through experimental cell system procedures.

Computational modelling and simulation deliver a faster, inexpensive and sustainable alternative for evaluating optimal reaction conditions. Application of computation in design and development of materials is coming as a promising tool. These computational and mathematical techniques may resolve many challenges such as parameters tuning associated with real experimental processes by predicting trends to be observed in synthesis and properties of hydrogel synthesized. They can also provide explanations of dynamics, thermodynamics and structure of hydrogel.

One versatile optimization technique is Data Envelopment Analysis (DEA). The traditional DEA has been reported to be exceptionally powerful model for recognizing the frontiers among multiple Decision-Making Units (DMUs) having various input and output yet with a weakness of discrimination inability. This inadequacy may be overwhelmed by different theoretical extensions to traditional DEA. Numerous such augmentations are Shannon's entropy, SBM-DEA model with weighting preference and slack based DEA model have been reported for detailed ranking of DMUs. The application of DEA is a fruitful approach for optimizing the reaction parameters of synthesis of hydrogel.

1.2 Work included

The work included in the thesis is the use of optimization techniques to find out the optimal parameters for the preparation of carboxymethyl tamarind kernel gum- poly vinyl alcohol hydrogel. Real time reactions were carried out by using CMTKG, PVA, sodium hydroxide, acrylic acid, potassium persulphate and N,N'-Methylenebisacrylamide and after that swelling studies were done and the result obtained were used for Data Envelopment Analysis optimization technique to identify the ideal reaction parameters. To get further knowledge, slack analysis has been done to report potential slacks in input parameters to increase the productivity of specific DMU. After optimizing the reaction parameters, the best DMU or the best sample was characterized using Fourier Transform Infrared Spectroscopy(FTIR), Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC). After characterization swelling studies were carried out at different temperature, pH and ionic solutions and the variations among these are reported.

Using such innovative computational approach for designing the precise synthesis hydrogels might be highly beneficial to save resources (chemicals), energy and time. Application of these techniques might be step forward to accomplish the objectives of green science.

Literature Review

This part of thesis includes an introduction to hydrogels along with its classification and introduction to carboxymethyl tamarind kernel gum (CMTKG) along with tamarind kernel gum (TKG), Tamarindus indica seeds from which it is extracted, poly vinyl alcohol, acrylic acid, initiator and crosslinker, rheology of hydrogel plus various computer modelling and simulations that have been reported/ used in this study for optimization of reaction parameters.

2.1 Introduction of hydrogels

Scientists, throughout the long term, have characterized hydrogels from numerous points of view. The most widely known out of these is that hydrogel is a water-swollen, and cross-linked polymeric network produced by reacting one or multiple monomers. One more definition is that it is a polymeric material that shows the capacity to swell and hold a huge amount of water inside its structure, yet won't dissolve in water. Hydrogels have gotten significant consideration in the previous 50 years, because of their exceptional response in various applications. They have additionally a level of adaptability fundamentally the same as characteristic tissue because of their huge water content. The capacity of hydrogels to absorb water emerges from hydrophilic functional groups attached to the polymeric spine, while their protection from disintegration emerges from cross-link between network chains. Numerous materials, both natural and manufactured, fit the meaning of hydrogels.

As of late, hydrogels have been characterized as two-or multicomponent frameworks comprising of a three-dimensional network of polymer chains and water that occupies the space between macromolecules. Contingent upon the properties of the polymer (polymers) used, just as on the nature and density of the network joints, such structures in an equilibrium can contain different measures of water; normally, in the swollen state, the mass fraction of water in a hydrogel is a lot higher than the mass fraction of polymer. Hydrogels might be synthesized in various "traditional" synthetic ways. These incorporate one-venture methods like polymerization and parallel cross-

linking of multifunctional monomers, just as different advance techniques including synthesis of polymer molecules having reactive groups and their ensuing cross-linking, perhaps at the same time by reacting polymers with suitable cross-linking agents. The polymer architect can plan and synthesize polymer networks with molecular scale authority over structure, for example, cross-linking density and with custom fitted properties, for example, biodegradation, mechanical strength, and chemical and biological response to stimuli.

2.1(a) Hydrogel as product sensitive to environmental conditions

As mentioned above, hydrogels as three-dimensional crosslinked hydrophilic polymer networks are capable of swelling or de-swelling reversibly in water and retaining large volume of liquid in swollen state. Hydrogels can be designed with controllable responses as to shrink or expand with changes in external environmental conditions. They may perform dramatic volume transition in response to a variety of physical and chemical stimuli, where the physical stimuli include temperature, electric or magnetic field, light, pressure, and sound, while the chemical stimuli include pH, solvent composition, ionic strength, and molecular species. The extent of swelling or de-swelling in response to the changes in the external environment of the hydrogel could be so drastic that the phenomenon is referred to as volume collapse or phase transition.

2.1(b) Hydrogel technical features

The functional properties of a hydrogel material is listed below :-

- The highest absorption capacity, maximum equilibrium swelling in distilled water.
- Desired rate of absorption (preferred particle size and porosity) depending upon the application required.

- It has lowest soluble content and residual monomer left.
- Cheaper
- Its durability and solubility is high.
- The highest biodegradability without formation of toxic species.
- pH-neutrality after swelling in water.
- Colorlessness, odor lessness, and absolutely non-toxic in nature.
- Photo stability.

Clearly, it is unimaginable that a hydrogel at the same time satisfy all the previously mentioned required highlights. In this way, practically speaking, the reaction variables should be optimized with the end goal that a suitable balance between the properties is accomplished. For instance, a hygienic product of hydrogels should have the highest absorption rate, the least re-wetting, and the least residual monomer, and the hydrogels utilized in medication conveyance should be permeable and responsive to one or the other pH or temperature.

2.2 Carboxymethyl Tamarind Kernel Gum (CMTKG)

CMTKG is an example of chemical modification from Tamarind Kernel gum. It contains D-xylose, D-galactose and D-glucose having molar ratio 1:2:3 [13]. It contains carboxymethylated chain of β-D-(1 → 4) linked with glucopyranosyl units along with the side chain containing single xylopyranosyl unit which are further attached with each 2nd, 3rd and 4th D-glucopyranosyl unit via α-D-(1 → 6) linkages and one xylopyranosyl unit is attached with one of the D- galactopyranosyl unit with a β-D-(1 → 2) linkage. The chemical structure of CMTKG.is shown below:

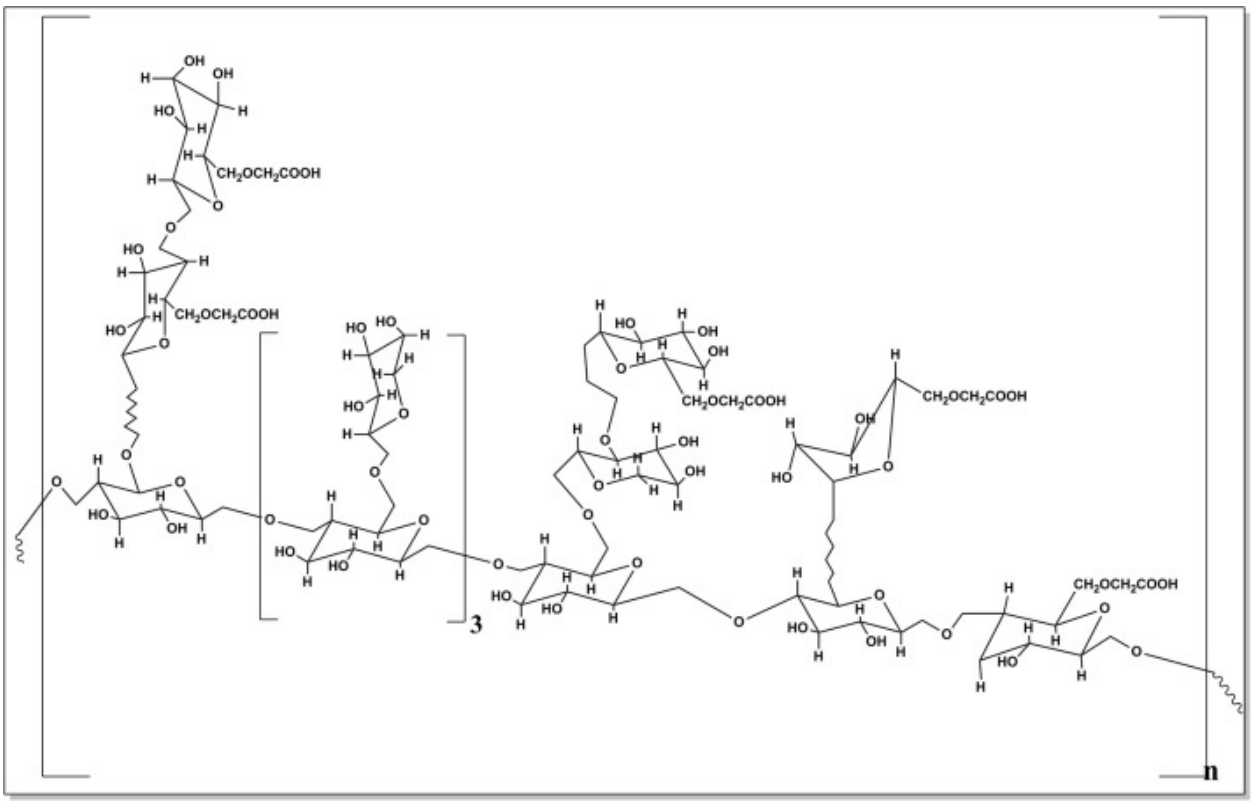

Fig 2 Chemical structure of CMTKG

Tamarind kernel gum (TKG) is amongst the cheapest gums available and it is a natural polysaccharide of food-grade which is extracted from the seeds of Tamarindus Indica L found in South East Asia and Africa [14]. The seeds contain xyloglucans which are usually used as gelling agents and food thickeners [15]. Although some of drawbacks of TKG are unpleasant odor, rapid biodegradability, limited solubility in cold water etc. [16] therefore modification is needed for

TKG to improve its pharmaceutical and physicochemical characteristics in order to increase its applicability [17]. Carboxymethylation of TKG upsets the polysaccharide structure, consequently uncovering the network of hydration and conferring an anionic nature to the polysaccharide. This chemical adjustment brings about lower biodegradability than TKG and accordingly improving the life shell, swell capacity, mucoadhesive, in situ gelation, wide pH resilience, high drug loading capacity, hydrophilicity. In addition to all the above expressed properties, CMTKG additionally shows antibacterial properties like that of TKG. In Fig. 3, unique properties of CMTKG and their importance has been featured.

Fig 3 Highlights of CMTKG

Throughout the long term, CMTKG has been utilized in fabricating composites, films, hydrogels, pellets, and so on which further been tried in different fields of use like horticulture, drug delivery, tissue engineering, wastewater treatment, and so forth The more in detail has been talked about and summed up beneath

Fig. 4. Various applications and forms of CMTKG.

2.3 Data Envelopment Analysis (DEA)

Charnes et al. (1978), developed the method, called as the Data Envelopment Analysis (DEA). This method is basically used for performance assessment. In the last few decades, studies like practical applications and theoretical developments have been published in literature. Since, DAE, after making limited assumptions and without specifying any functional form in advance, easily deal with multi-input multi-output production technologies. The DEA has additionally opened up opportunities for application in cases that were not viable with different methodologies because of the complex (often unknown) nature of the relations between the multiple inputs and multiple outputs associated with decision making units (DMUs).

A guideline, that the quantity of units ought to be in any event double the quantity of data sources and yields, ie. input and output values, was established by Roll & Golany (1989) [21]. Boussofiane et al. (1991) mentioned that to get good differential power out of the BCC and CCR models the lower bound on the number of DMUs should be the multiple of the number of outputs and the number of inputs [20]. The number of DMUs to that of output and input values should be thrice was published by Bowlin (1998) [22]. However, in 2001 Dyson et al. suggested that the number of DMUs should be two times to the product of the number of output and input variables [23].

With extra-enormous informational collections, some investigations may wish to lessen the size by taking out the connected factors of output and input. This saved some time in information procurement, calculation, and storage, yet the huge admonition was that after incorporation of a completely connected factor, the model may yield a somewhat different outcome. The precision of the outcomes may rely upon the degree of connection that is worthy. Since its presentation in 1978, scientists in different fields have immediately perceived DEA as a successful and advantageous instrument for demonstrating operational cycles for execution assessments (Yadav et al., 2010, 2011; Ghosh et al., 2018) [24].

First model of DEA was introduced by Charnes et al. (1978) built on elementary formulation of Farrell (1957) that enabled the determination of a unit's efficiency based on its inputs and outputs, and compared it to other units involved in the analysis. The different classic DEA models assumed to be either input or output oriented. In input-oriented DEA models, inputs were minimized while keeping the outputs constant, whereas on output oriented DEA models, outputs were maximized

keeping inputs unchanged (Coelli, 1996) [25]. However, in BCC (Bankers, Charnes, Cooper) DEA model, the outcome of input and output oriented models were different, while in the case of CCR (Charnes, Cooper, Rhodes) DEA model, it remained similar. Recently published research work in different fields that applied DEA optimization technique have been included in subsequent paragraphs.

Han et al. (2020) worked on Data Envelopment Analysis (DEA) cross model integrated interpretive structural model and analytic hierarchy process for energy efficiency evaluation and optimizing modelling, respectively [26]. The interpretive structural model was used to reduce the multi-dimensional indicators that influence the DEA model and were projected before DEA as input indicators with ethylene yield as output parameters to evaluate the efficiency of ethylene production plants. Sarraf & Nejad (2020) evaluated the efficiencies of 35 water and waste water companies in Iran by utilizing DEA as a tool and also proposed Grey relational analysis (GRA) to evaluate the performance of these companies [27]. Results revealed that GRA outperforms when compared to DEA. A complete literature survey on applications of DEA in the insurance companies in terms of years, countries and regions were discussed by Kaffash et al. (2019) [28]. DEA was used to estimate the efficiency of greenhouse farmers and pinpoint the wasted resources. The socioeconomic factor that has the most positive effect on greenhouse efficiency was the secondary occupation of the farmer; especially when that occupation pertained to the government agricultural sector (Al-Mezeini et.,2020) [29]. Even with the use of data pre-processing tools, it often becomes a huge matrix in terms of dimension variables. Zelenyuk (2020), proposed price based aggregation as a solution to address the problem of very large dimensions [30].

Charles et al. (2019) proposed a simple approach to increase the discriminatory power between efficient and inefficient DMUs using the well-known pure DEA model [31]. Peyrache et al., (2020) introduced cardinality constraints that could be used directly in DEA in order to select the relevant inputs and outputs automatically. The performance of Public Higher Education Institutions (PHEI) in terms of three activities namely teaching, research and knowledge dissemination was evaluated using DEA. Moncayo-Martineza et al. (2020) evaluated the efficiency of 40 Mexican PHEI from the year 2008-2016.

Atris (2020) examined the efficiency-based ranking for oil and gas refineries using DEA and discriminant analysis [32]. A Kruskai-Wallis rank sum test was conducted to examine whether the

average efficiency-based ranks could measure change over time and whether they differed among the four different regions (U.S. and Canada; Europe; Asia Pacific; and Middle East) for the years between 2007 and 2018. Ullah et al. (2019) applied the DEA for the efficiency evaluation of different sugarcane production systems of Thailand situated in various regions of the country. DEA provided a platform to improve the performance of the plants through the reduction in the current pattern of farm inputs in the various regions.

Chu et al. (2019) proposed a new approach for addressing the non-Pareto optimality problem in data envelopment analysis (DEA) cross-efficiency evaluation. A multi objective model with a new non-self-denial weight-selection principle was proposed to obtain Pareto-optimist cross-efficiency scores. The sum weighted approach was utilized to evaluate the multi-objective model. Further, Pareto optimal cross efficiency scores were obtained by using common weight evaluation results.

Yu et al. (2019) proposed another method of developing the non-covex meta-system of the unique network data envelopment investigation. This new methodology varies from the base extrapolation rule on the conglomeration of individual group innovations. The new SBM DEA models change unique negative information sources and yields into positive partners dependent on a recently defined "base point". Pambudi and Nananukul (2019) proposed a progressive fluffy data envelopment examination model for recognizing appropriate areas for the development of wind ranches in Indonesia. Assessments from specialists in various territories were gathered and addressed by the reluctant fluffy phonetic term sets, which were changed over to idealistic and cynical inclinations by utilizing etymological accumulation and later incorporated to the data envelopment investigation model.

Gobbi et al. (2019) employed the DEA to analyze different port areas in terms of plastic segregation and amount of plastic is recycled. Top et al. (2020) employed DEA to measure the efficiencies of health care systems of 36 African countries. It was concluded that the national health care systems need to use public and private health Resources more effectively. Iyer & Jain (2019) evaluated the performance of 61 airports across the globe during 2009-2017. Authors analyzed the performances and associations made with obtained efficiency scores. On the other hand, the features (input and output) selection was proposed by Benitez-Pena et al. (2019). The DEA model was enriched with zero one decision variables forming a mixed integer linear programming approach for the application. The performances of chemical universities of the country UK were

evaluated using DEA proposed by Gosalez-Garay et al. (2019) by using the data retrieved from two national rankings.

Wang et al. (2019) evaluated the performance of China's iron and steel industry using DEA. Results of various models like CCR, BCC were compared and analyzed. Finally, a regression model was utilized to investigate the key environmental protection strategies Influencing environmental efficiency. Luo et al. (2019) proposed a Malmquist index and DEA to evaluate the efficiency of green technology innovation in strategic emerging industries. Ang et al. (2018) employed DEA to evaluate the performance of hotels under the tourism industry and presented group efficiency and group cross efficiency to evaluate the Taiwan hotel chains and subsidiary hotels by collecting the data from 2011 to 2015 [34].

Despite having so many advantages, classical DEA models have following shortcomings; firstly, it provided only dichotomized classification of data sets, i.e. Efficient or inefficient DMUs. Hence several DMUs might be classified as the efficient ones. This made identification of the best performing DMUs difficult amongst the set of efficient DMUs. Secondly, the classification between the efficient and inefficient DMUs might vary with different DEA models. Hence, identification of DMUs as efficient or inefficient ones would depend on choice of models in analysis based on classical DEA models.

Experimental

3.1 Material required: -

- Carboxymethyl tamarind kernel gum (CMTKG)
- Poly vinyl alcohol cold (PVA)
- Sodium hydroxide (NaOH)
- Acrylic Acid
- Potassium persulphate (KPS)
- N,N'- Methylenebisacrylamide (MBA)
- Distilled water
- Breakable test tubes
- Water bath
- Magnetic stirrer

Carboxymethyl tamarind kernel gum (CMTKG)

CMTKG was given by Hindustan Gum and chemicals ltd., Bhiwani, Haryana

Sodium hydroxide (NaOH)

Sodium hydroxide in the form of pellets were used which were further dissolved in distilled water in desired proportion manufactured by Thermo Fisher Scientific India Pvt. Ltd Powai, Mumbai.

Acrylic Acid

Acrylic acid pure from Sisco Research Laboratories Pvt. Ltd is dissolved in mixture of sodium hydroxide and distilled water in order to convert into sodium acrylate.

Polyvinyl alcohol (cold)

White crystalline powder of polyvinyl alcohol manufactured by Central Drug House Pvt. Ltd, New Delhi was taken.

Potassium persulphate

Potassium persulphate from Thomas Baker (chemicals) limited, Mumbai was used as an initiator in the reaction system for synthesis of hydrogel.

N,N'- Methylene-diacrylamide

N,N'-Methylene-diacrylamide (MBA) from Merck Schuchardt OHG 85662 Hohenbrunn, Germany was used as a cross linker for synthesis of hydrogel in the reaction system.

3.2 Procedure for Synthesis of Hydrogel

- First of all, 10ml of distilled water was taken in a 100 ml beaker which was kept on magnetic stirrer at room temperature, 300rpm and desired amount of CMTKG (0.1, 0.2, 0.3 and 0.4 g) was added.
- In another beaker, 8ml of distilled water with 2.5g of NaOH is mixed until NaOH pellets get dissolved. Once the pellets got dissolved completely 4.5ml of Acrylic acid was poured into it with constant stirring at 400 rpm for about 30 mins.
- On completion of 30 mins the above neutralized sodium acrylate solution was poured into the beaker having CMTKG in it with a constant stirring at 300 rpm for another 30 mins
- Meanwhile in another beaker desired amount of Polyvinyl alcohol was mixed with 8ml of distilled water until it got dissolved completely on magnetic stirrer at 400 rpm and room temperature
- Once the solution of CMTKG and sodium acrylate is mixed for 30 mins then Polyvinyl alcohol which was in another beaker was added to the reaction system and it was stirred for another 30 mins.
- After 30mins of PVA mixing the initiator Potassium persulphate (KPS) in desired proportion was added to the reaction system along with continuous stirring for another 20 mins.
- After 20 mins of mixing the cross linker MBA in desired proportion was added to the reaction system with continuous stirring for 40mins to ensure a uniform suspension before it is poured into the test tube.
- Then the final solution formed is poured into the test tube and was placed in the water bath for solidification at 60ºC for 2 hours.

- The solidified hydrogel formed is taken out by breaking the test tube and is then cut into thin slices of about 1cm.
- These thin slices or disc shaped hydrogel is dipped inside distilled water for around 12hrs in order to remove impurities and unreacted materials.
- The overnight swollen hydrogels were then air dried for around 3 days after which they were dried in oven at 40^{o} C till constant weight.

Fig 5 Dried hydrogel (diameter 0.89cm, thickness 0.435cm)

Fig 6 Swollen hydrogel (diameter 5.09cm, thickness 2.56cm)

The diameter of swollen hydrogel is increased by 472% and thickness is increased by 489%.

3.3 Data Envelopment Analysis

Total 16 samples were synthesised by varying the reaction parameters and the result obtained were then entered in DEA Solver Light Version 8 to get the optimized output or the optimized reaction parameters on which the further studies were done

3.4 SWELLING STUDIES

Water studies of synthesized hydrogel were done by using the given below formula. Weight of fully dried hydrogel samples were carefully taken and then they were immersed in different mediums like distilled water, solutions having different pH, standard saline solution, ionic solutions and the weight of swollen hydrogels were taken and swelling index was calculated.

$$\mathbf{SD= (Wesh – Wdh)/Wdh}$$

where, SD is the swelling index of hydrogel, Wesh is the weight of swollen hydrogel at equilibrium while Wdh is the initial weight of the dried hydrogel.

Also swelling studies were done for different ionic solutions and the response was studied by allowing the hydrogel to swell in various ionic mediums.

0.1 M NaCl solution

For making 0.1 M NaCl solution, 2.922g of NaCl was dissolved in 500ml water and then the hydrogel was dipped inside the ionic medium and swelling behavior was observed.

0.1 M Magnesium Sulphate solution

For making 0.1 Molar $MgSO_4.7H_2O$, 12.324g magnesium sulphate was dissolved in 500ml water.

0.1 M Aluminum Sulphate solution

For making 0.1 Molar aluminum sulphate solution, 31.52g of aluminum sulphate was dissolved in 500ml water.

3.5 Rheological studies

Rheological measurements were of swollen hydrogels were carried out on a rotational rheometer, Anton Paar Modular Compact Rheometer MCR 302. All rheology measurements were made using a 25mm diameter spindle and plane geometry. The temperature was controlled at 25 degree Celsius with the help of chiller. The samples were carefully placed on the surface of lower plate and the upper spindle was lowered to a 0.052 mm gap distance. Before testing, samples were left equilibrating for ten minutes in order to allow mechanical and temperature equilibrium.

For oscillatory tests, an amplitude sweep was carried out at frequency of 10/s and shear strain ranging from 0.001 to 15 for both distilled water and saline solution. Frequency sweep was carried for both distilled water and saline solution.

3.6 Characterization

Fourier-transform infrared (FTIR) spectroscopy

The FTIR spectra of CMTKG-PVA based optimized hydrogel was recorded using a FTIR spectrophotometer in a solid-state using ATR mode on FTIR (Niclot 6700).

Thermal analysis

The thermo-gravimetric analysis (TGA) of CMTKG-PVA hydrogel was carried out using a PerkinElmer TGA in presence of N2 atmosphere from 25 °C to 900 °C with 10 °C/min of uniform heating rate.

Scanning electron microscopy (SEM)

Surface morphology of CMTKG-PVA hydrogel was analyzed by SEM Zeiss EVO 50 & EVO 18 Special and results are discussed in next chapter.

Result and discussion

4.1 Swelling results

SAMPLE	(I) CMTKG	(I)AA	(I)NaOH	(I)PVA	(I)KPS	(I)MBA	(O)SWELLING
1	0.1	4.5	2.5	0.1	0.1	0.1	56.732
2	0.2	4.5	2.5	0.1	0.1	0.1	59.936
3	0.3	4.5	2.5	0.1	0.1	0.1	71.966
4	0.4	4.5	2.5	0.1	0.1	0.1	88.536
7	0.1	4.5	2.5	0.05	0.1	0.1	108.023
8	0.1	4.5	2.5	0.025	0.1	0.1	113.922
9	0.1	4.5	2.5	0.075	0.1	0.1	73.291
10	0.1	4.5	2.5	0.1	0.1	0.05	130.34
11	0.4	4.5	2.5	0.1	0.1	0.05	89.32
12	0.1	4.5	2.5	0.1	0.1	0.2	49.22
13	0.1	4.5	2.5	0.1	0.1	0.3	30.064
14	0.1	4.5	2.5	0.1	0.1	0.4	28.203
15	0.1	4.5	2.5	0.1	0.2	0.1	82.206
16	0.1	4.5	2.5	0.1	0.3	0.1	80.577

Table 1 swelling results

4.1(a) Effect of CMTKG concentration

As shown in the table above as we increase the concentration of CMTKG from 0.1g to 0.4g in sample 1 to 4 the swelling index increases due to the COO^- groups and the number of counter ions (Na^+) along the polymeric network also increased within the gel phase, resulting into an amplification in the chain relaxation because of the repulsion occurring among like charged COO^- groups. Furthermore, osmotic swelling pressure too got increased because of the increase in Na^+ (free counter ions) in the gel phase. Hence, these two factors play a major part towards the increased swelling index of SAH with respect to the concentration of CMTKG [19].

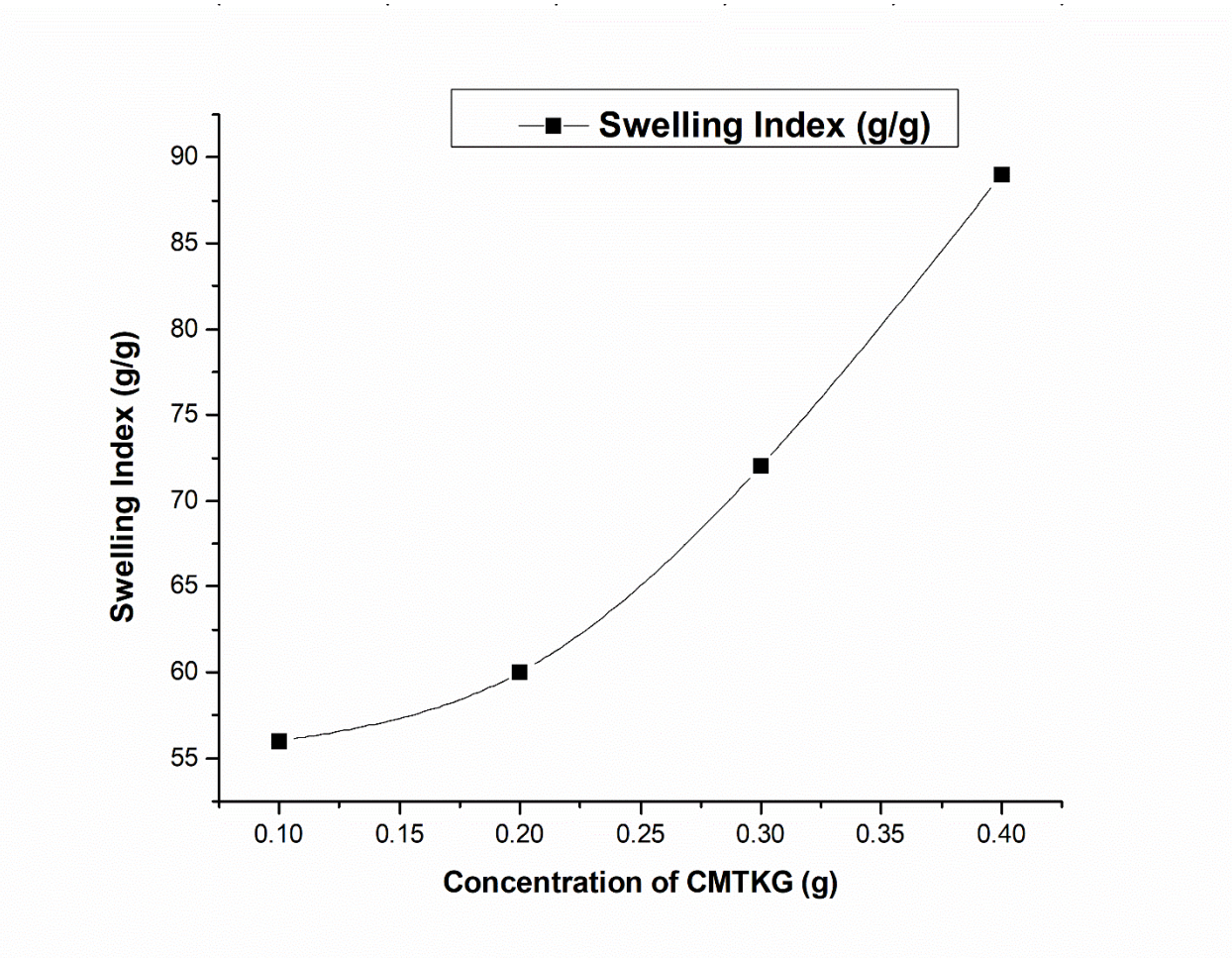

Fig 7 Effect of CMTKG concentration

4.1(b)Effect of varying the concentration of Polyvinyl alcohol

It is evident from the above data shown in the figure 6 as we decrease the concentration of polyvinyl alcohol in sample 1, 7, 8, 9 our swelling index increased or we can say that on increasing the concentration of PVA the swelling behavior decreases as increasing the concentration of PVA leads to a more homogeneous and denser hydrogel structure with significantly lower equilibrium swelling. Also we came to know that on increasing the concentration of PVA we need to decrease the concentration of MBA so as to maximize the swelling which is proved in slack analysis below.

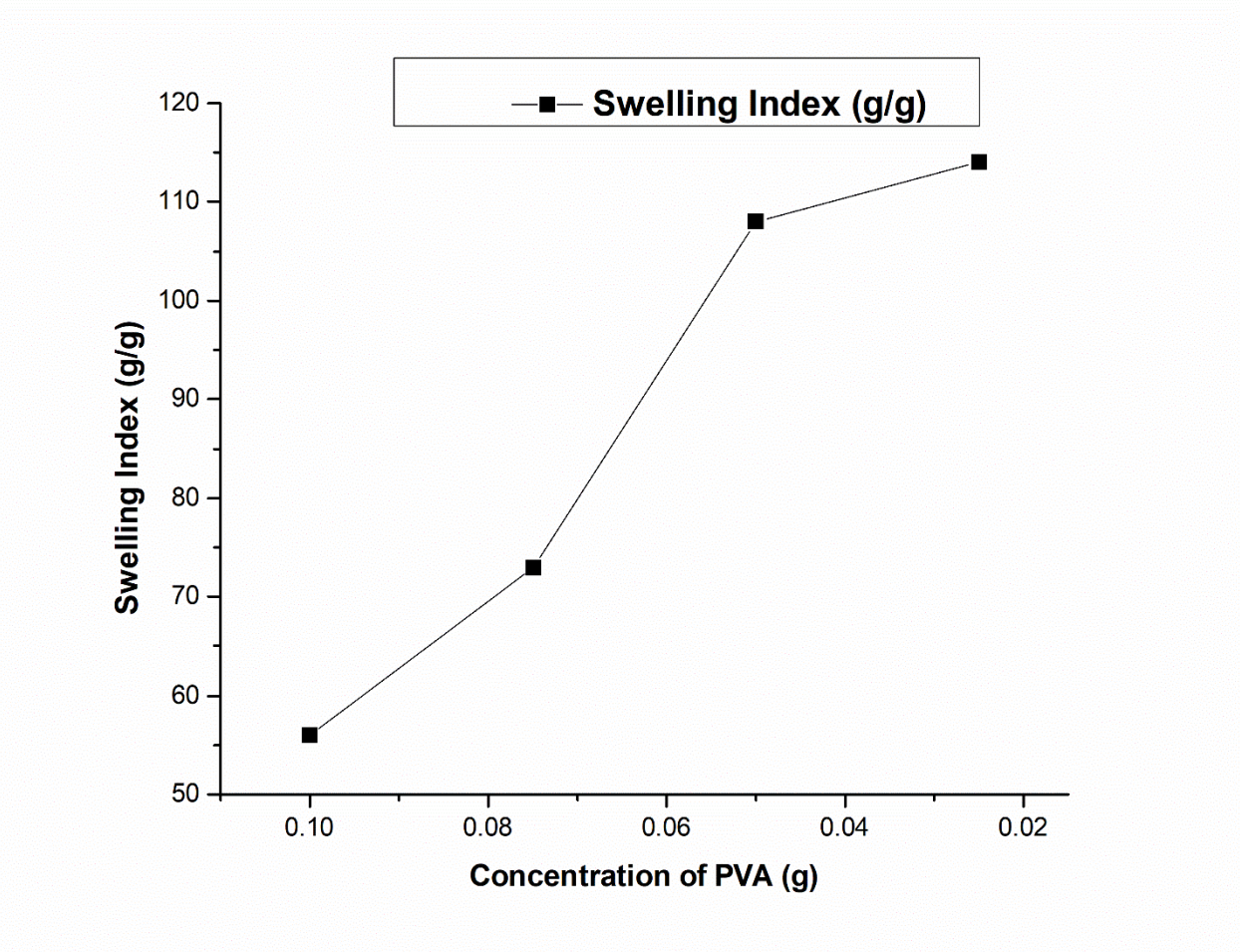

Fig 8 Effect of varying the concentration of Polyvinyl alcohol

4.1(c)Effect of concentration of Cross-linker

On increasing the concentration of cross-linker the swelling index or the swelling properties of hydrogel diminishes significantly. Cross-linking density is one of the significant factors which influences swelling of SAH as clarified by Flory's network hypothesis [28]. Taking into account the swelling of SAH, the connection between the swelling and the concentration of cross-linker, MBA was examined. As the concentration of MBA increased from 0.05g to 0.4g the swelling diminished significantly. It is realized that the amount of cross-linker decides the cross-connecting density. Thus, higher the concentration of MBA levels, more will be the cross-

linking, which brought about additional network formulation. Therefore, the pore spaces among the framework of the tri-dimensional network would diminish which further decreased the free volume available inside the polymeric network of hydrogel, and confining the water absorption rate. Hydrogels become harder and stiffer with excess cross-connecting. It was seen that the hydrogel with much lesser concentration than 0.05g came about into the development of jelly like product. This can be credited to the insignificant network formation between the chains of polymers.

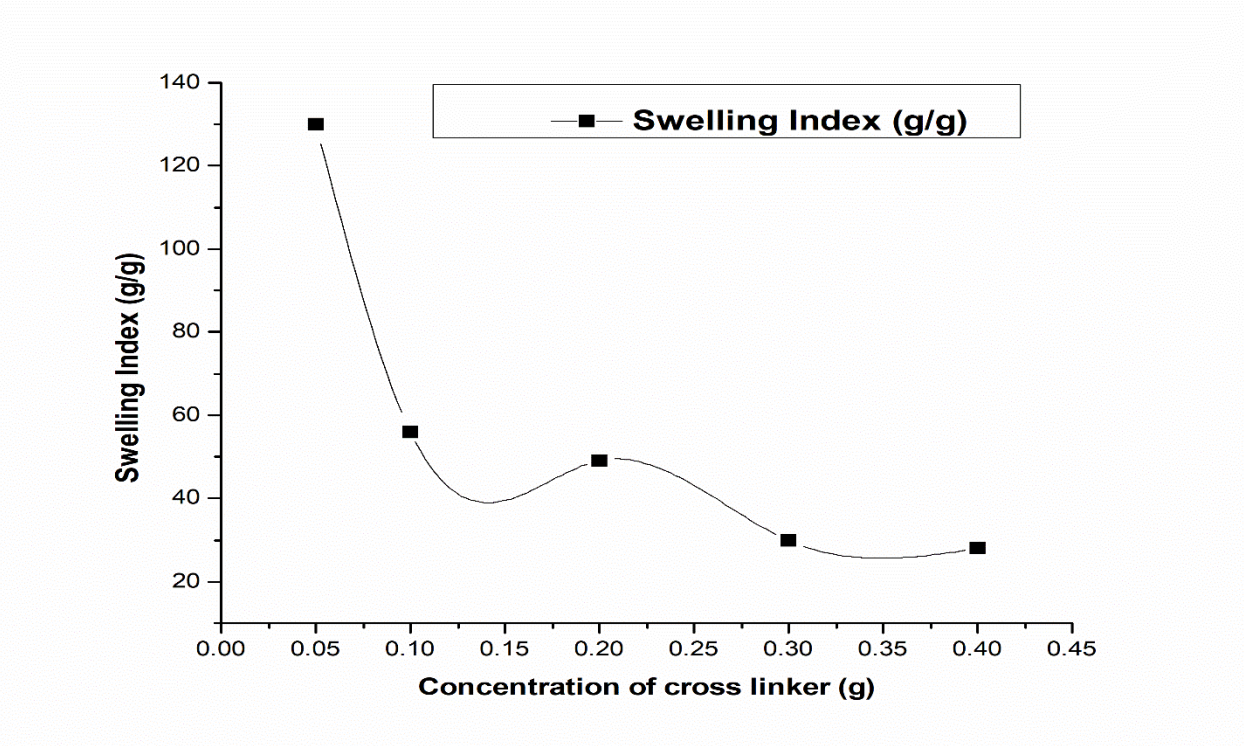

Fig 9 Effect of concentration of Cross-linker

Also during synthesis, we found that on increasing the concentration of PVA above 0.1g in sample 5 and 6 there was residue or unreacted PVA left which got settled at the bottom of the test tube so we got to know that 0.1g is the limiting value for PVA concentration. Sample 11 was also not dimensionally stable due to maximum concentration of CMTKG which is 0.4g.

4.2 Optimization results

DEA model = DEA-Solver LV8.0/ CCR(CCR-O)
Problem = SAMPLE
No. of DMUs = 14

No. of Input items = 6
Input(1) = CMTKG
Input(2) = AA
Input(3) = NAOH
Input(4) = PVA
Input(5) = KPS
Input(6) = MBA
No. of Output items = 1
Output(1) = SWELLING

Statistics on Input/Output Data

	CMTKG	AA	NAOH	PVA	KPS	MBA	SWELLING
Max	0.4	4.5	2.5	0.1	0.3	0.4	130.34
Min	0.1	4.5	2.5	0.025	0.1	0.05	28.203
Average	0.16429	4.5	2.5	0.08929	0.12143	0.13571	75.8811429
SD	0.11089	0	0	0.02259	0.05579	0.0953	28.7538606

Correlation Data

	CMTKG	AA	NAOH	PVA	KPS	MBA	SWELLING
CMTKG	1	0	0	0.275	-0.2227	-0.3187	0.1221061
AA	0	1	0	0	0	0	0

NAOH	0	0	1	0	0	0	0
PVA	0.275	0	0	1	0.1822	0.17777	-0.48339549
KPS	-0.2227	0	0	0.1822	1	-0.144	0.06998367
MBA	-0.3187	0	0	0.17777	-0.144	1	-0.76970796
SWELLING	0.12211	0	0	-0.4834	0.06998	-0.7697	1

Table 2

No. of Efficient DMUs = 2
No. of Inefficient DMUs = 12

4.2(a)Weighted data

DMU	Score	Rank		v(1)*CMTKG	v(2)*AA	v(3)*NAOH	v(4)*PVA	v(5)*KPS	v(6)*MBA		u(1)*SWELLING
1	0.4353	11		0	0	0	0	2.2974688	0		1
2	0.4598	10		0	0	0	0.365234	1.8094189	0		1
3	0.5521	9		0	0	0	0	1.811133	0		1
4	0.6793	5		0	1.47217	0	0	0	0		1
7	0.9048	3		0	0	0	0.101324	1.0039467	0		1
8	1	1		0.951961283	0	0	4.80E-02	0	0		1
9	0.587	8		0	0	0	0.224011	1.4797087	0		1
10	1	1		0	0	0	0	1	0		1
11	0.6853	4		0	0	0	0	0	1.45924765		1
12	0.3776	12		2.648110524	0	0	0	0	0		1
13	0.2307	13		4.335417775	0	0	0	0	0		1
14	0.2164	14		4.621494167	0	0	0	0	0		1
15	0.6307	6		1.585529037	0	0	0	0	0		1
16	0.6182	7		1.617583181	0	0	0	0	0		1

Table 3

Score and rank of all the DMUs

DMU	Score	Rank
8	1	1
10	1	1
7	0.9048	3
11	0.6853	4
4	0.6793	5
15	0.6307	6
16	0.6182	7
9	0.587	8
3	0.5521	9
2	0.4598	10
1	0.4353	11
12	0.3776	12
13	0.2307	13
14	0.2164	14

Table 4

Graph showing relative efficiencies of various DMUs

Sample 8 and 10 are lying on the efficiency frontier and hence given rank 1 and are termed as efficient DMUs rest all are lying below it and are getting the score less than 1. Sample 14 is the worst DMU as it is consuming excess amount of resources still giving least output which is swelling.

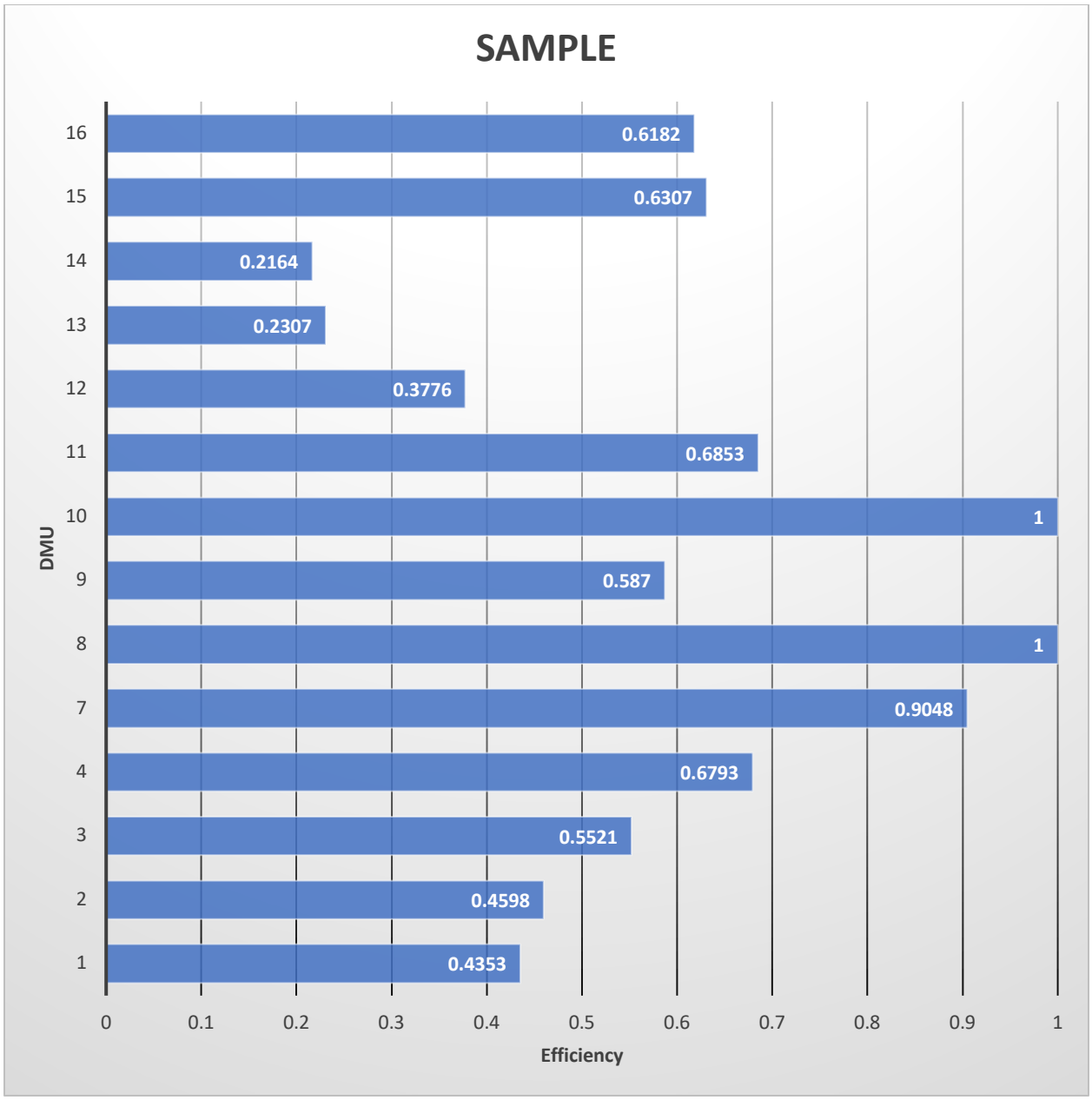

Fig 10 Relative efficiency

As shown in the graph above sample 8 and 10 are having relative efficiency of 100 percent and rest are compared with respect to them as they lie on the efficiency frontier and rest all others DMUs lie inside the efficiency frontier according to DEA analysis.

Projected data

			CMTKG			AA			NAOH			PVA			KPS			MBA		
DMU	Score	Rank	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)
1	0.4353	11	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.1	0.05	-50
2	0.4598	10	0.2	0.1	-50	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.1	0.05	-50
3	0.5521	9	0.3	0.1	-66.667	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.1	0.05	-50
4	0.6793	5	0.4	0.1	-75	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.1	0.05	-50
7	0.9048	3	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.05	0.05	0	0.1	0.1	0	0.1	0.08333	-16.667
8	1	1	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.025	0.025	0	0.1	0.1	0	0.1	0.1	0
9	0.587	8	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.075	0.075	0	0.1	0.1	0	0.1	0.06667	-33.333
10	1	1	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.05	0.05	0
11	0.6853	4	0.4	0.1	-75	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.05	0.05	0
12	0.3776	12	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.2	0.05	-75
13	0.2307	13	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.3	0.05	-83.333
14	0.2164	14	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.1	0.1	0	0.4	0.05	-87.5
15	0.6307	6	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.2	0.1	-50	0.1	0.05	-50
16	0.6182	7	0.1	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.3	0.1	-66.667	0.1	0.05	-50

			CMTKG			AA			NAOH			PVA			KPS			MBA		
	Score	Rank	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)	Data	Projection	Diff.(%)
Average	0.5984	7.4286	0.1643	0.1	-19.048	4.5	4.5	0	2.5	2.5	0	0.0893	0.0893	0	0.1214	0.1	-8.3334	0.1357	0.0571	-42.56
Max	1	14	0.4	0.1	0	4.5	4.5	0	2.5	2.5	0	0.1	0.1	0	0.3	0.1	0	0.4	0.1	0
Min	0.2164	1	0.1	0.1	-75	4.5	4.5	0	2.5	2.5	0	0.025	0.025	0	0.1	0.1	-66.667	0.05	0.05	-87.5
St Dev	0.2496	4.2916	0.1151	0	31.7625	0	0	0	0	0	0	0.0234	0.0234	0	0.0579	0	21.4337	0.0989	0.0156	29.4255

Table 5

This data shows the difference between the actual data we have taken in synthesis of various samples and the projected data which should be used in order to make all the DMUs efficient or to make them lie on the efficiency frontier so this kind of analysis helped in increasing the relative efficiency of inefficient DMUs and help to make them efficient too. Basically, in this analysis the DEA compares the data we have taken in the reaction parameters to what it ideally should be according to DEA in order to make it efficient so this helps in figuring out where we are lagging and helps in making an inefficient DMU an efficient one.

4.2(b)Slack analysis

			Slack	Slack	Slack	Slack	Slack	Slack	Slack
DMU	Score	Rank	CMTKG	AA	NAOH	PVA	KPS	MBA	SWELLING
1	0.4353	11	0	0	0	0	0	0.05	0
2	0.4598	10	0.1	0	0	0	0	0.05	0
3	0.5521	9	0.2	0	0	0	0	0.05	0
4	0.6793	5	0.3	0	0	0	0	0.05	0
7	0.9048	3	0	0	0	0	0	0.017	0
8	1	1	0	0	0	0	0	0	0
9	0.587	8	0	0	0	0	0	0.033	0
10	1	1	0	0	0	0	0	0	0
11	0.6853	4	0.3	0	0	0	0	0	0
12	0.3776	12	0	0	0	0	0	0.15	0
13	0.2307	13	0	0	0	0	0	0.25	0
14	0.2164	14	0	0	0	0	0	0.35	0
15	0.6307	6	0	0	0	0	0.1	0.05	0
16	0.6182	7	0	0	0	0	0.2	0.05	0

	Score	Rank	CMTKG	AA	NAOH	PVA	KPS	MBA	SWELLING
Average	0.5984	7.4286	0.0643	0	0	0	0.0214	0.0786	0
Max	1	14	0.3	0	0	0	0.2	0.35	0
Min	0.2164	1	0	0	0	0	0	0	0
St Dev	0.2496	4.2916	0.1151	0	0	0	0.0579	0.1028	0

Table 6

Slack analysis is a gift of DEA towards green chemistry as through this analysis in synthesis we got to know that what proportions or amount is there in excess in each DMU which we can focus upon and reduce it in order to make that inefficient DMU an efficient one as explained below sample wise. Also, by knowing the excess amount used we can minimize the wastage and thus properly utilize the resources in order to achieve the goals of green chemistry.

Sample 1

In sample 1 there is slack in concentration of cross linker MBA which is 0.05 which means if we reduce the concentration of cross linker by 0.05g then we will get maximum swelling from this combination or we can say that 0.05g of MBA is excess in sample 1 which is not helping us in anyway to achieve optimum results and is termed as waste so we need to reduce this amount so as to make it optimum.

Sample 2

In sample 2 there is slack of 0.1g of CMTKG and slack of 0.05g of MBA which means 0.1g of CMTKG is extra and is termed as waste which we can reduce plus 0.05g of MBA is also in excess which is restricting its swelling hence need to reduce it.

Sample 3

In sample 3 there is slack of 0.2g of CMTKG and 0.05g of MBA which means 0.2g of CMTKG is extra and is termed as waste which we can reduce plus 0.05g of MBA is also in excess which is restricting its swelling hence need to reduce it.

Sample 4

In sample 4 there is slack of 0.3g of CMTKG and 0.05g of MBA which means 0.3g of CMTKG is extra and is termed as waste which we can reduce plus 0.05g of MBA is also in excess which is restricting its swelling hence need to reduce it.

Sample 7

In sample 7 there is only one slack which is 0.017g of MBA which we need to decrease in order to make it efficient. In this sample we have decreased the concentration of PVA to 0.05g and this is the reason that just 0.017g of MBA is excess in comparison to previous 0.05 as decrease in PVA concentration also help in increasing the swelling index.

Sample 8

This sample according to DEA lie on efficiency frontier and hence is termed as efficient and there is no slack in this reaction parameters. In this sample we have used cross linker 0.1g still these parameters are optimized which is due to the decreased or minimum concentration of PVA which also helped in increasing the swelling index.

Sample 9

In this sample there is slack of 0.033g of MBA as in this sample the concentration of PVA is 0.075g which is slightly increased in comparison to sample 7 where it was 0.05g and hence due to which the slack of MBA is increased from 0.017g to 0.033g which suggest if we are increasing the concentration of PVA then we need to decrease the cross-linker concentration in order to maximize the sweeling.

Sample 10

This sample according to DEA lie on efficiency frontier and hence is termed as efficient and there is no slack in this reaction parameters. In this sample we are using 0.1g of PVA still it is lying on efficiency frontier due to decreased concentration of MBA which we have used is minimum less than that gel formation did not take place.

Sample 11

In this sample there is slack of 0.3g of CMTKG which is making it dimensionally unstable and hence not getting the desired result with this much cross linker concentration of 0.05g.

Sample 12

In this sample there is slack of 0.15g of MBA which is high and hence restricting its sweeling behaviour.

Sample 13

In this sample there is slack of 0.25g of MBA which is high and hence restricting its sweeling behaviour so need to reduce it as it is not helping our cause.

Sample 14

In this sample there is slack of 0.35g of MBA which is very high and hence restricting its sweeling behaviour so need to reduce it as it is not helping our cause and is going as a waste.

Sample 15

In this sample there is slack of 0.1g of KPS which is the initiator as 0.1g of initiator is sufficient to give desired results and 0.05g of MBA is also excess which is further decreasing its swelling.

Sample 16

In this sample there is slack of 0.2g of KPS which is the initiator as 0.1g of initiator is sufficient to give desired results and 0.05g of MBA is also excess which is further decreasing its swelling.

4.3 Swelling studies in ionic medium

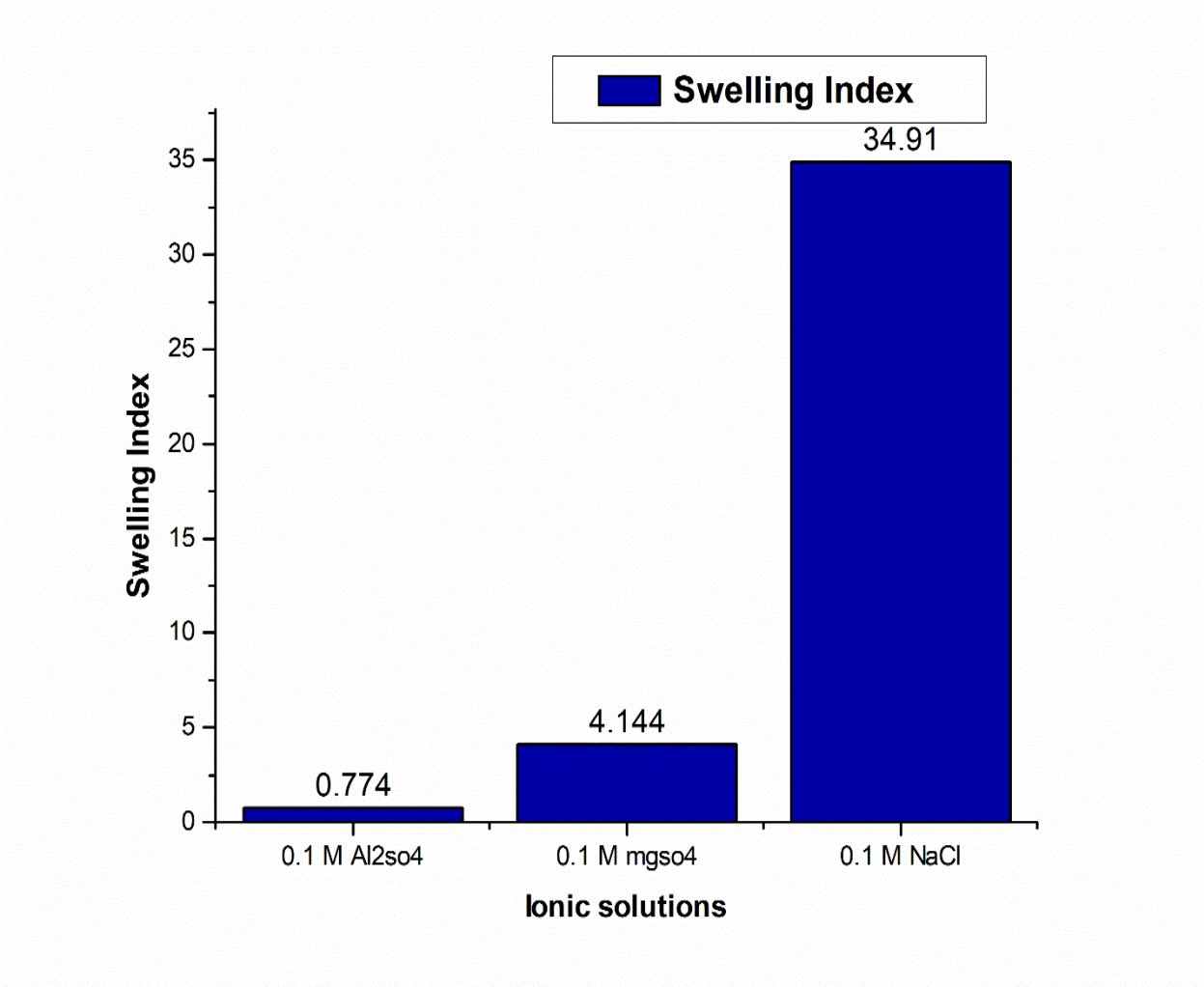

Fig 11 Swelling studies in ionic medium

It is shown in the graph that as we move towards right in periodic table, our atomic number increases and the swelling index decreases. As the readings were taken after 24hr and for NaCl it is 34.91, for magnesium sulphate it is 4.144 and for aluminium sulphate it is 0.774. The reduced water uptake in salt solutions is often attributed to the decline of osmotic pressure between the gel network and external solution due to increase in ionic strength and also due to the increase of screening effect of counter ions. So it is evident from the above figure that percent swelling of hydrogel in different electrolyte solution follow the order $Na^{+} > Mg^{2+} > Al^{3+}$. Unlike monovalent cation, multivalent cation form ionic crosslink with anionic hydrophilic groups, this is the reason behind reduced swelling tendency in $MgSO^{4}$ and $AlSO^{4}$ than in NaCl solution.

4.4 Swelling with time in distilled water of optimized hydrogel

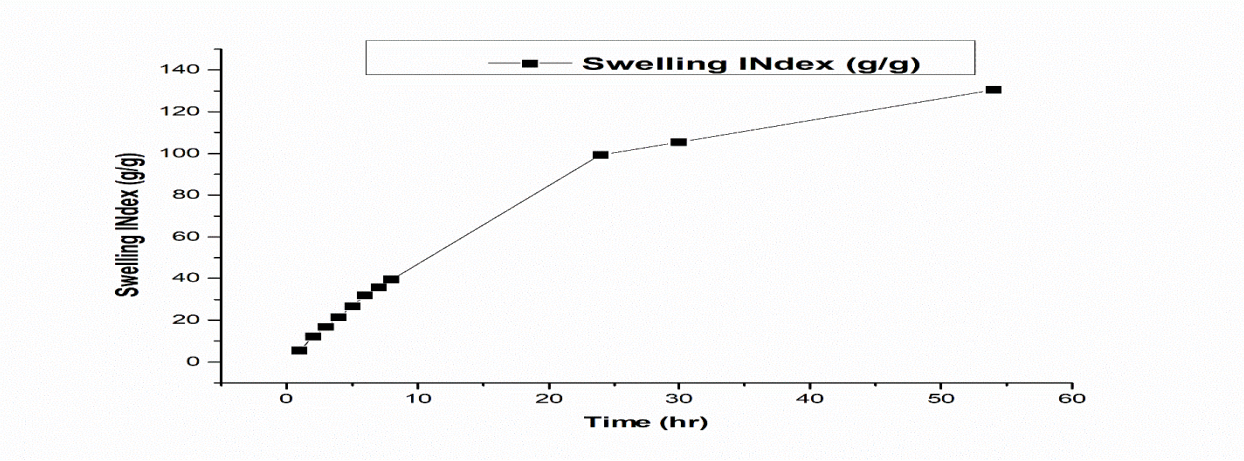

Fig 12 Swelling with time in distilled water of optimized hydrogel

In the above graph the swelling behaviour of optimized hydrogel was studied with time, initially eight readings were taken in one hour interval continuously for eight hours and then was evaluated after 24hr, 30hr and then finally equilibrium was reached after 54hr of swelling and the swelling index of 130.34% was reached after which the swelling index did not increased much hence it was equilibrium swelling.

4.5 Absorption studies in different solvents

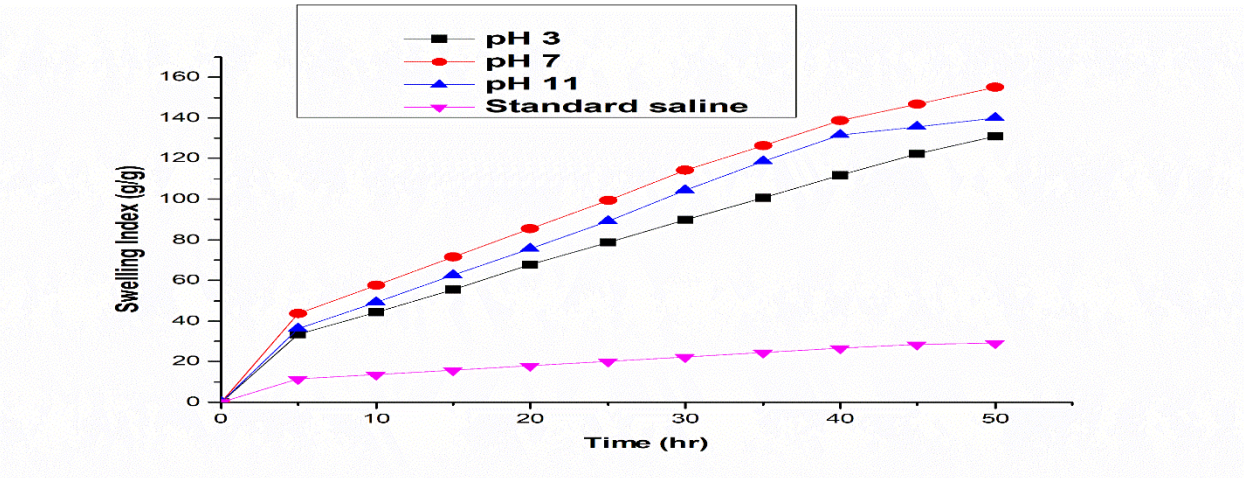

Fig 13 Absorption studies in different solvents

In this graph the swelling behaviour of hydrogel in different solution is shown in which the max swelling index is for solution having pH 7, lowest is for saline solution.

Also we came to know that as pH increases from acidic to basic medium swelling index also increases till 7 but above that when we observed it for pH 11 then the swelling decreases, the reason behind the lesser amount of swelling is the increase in alkalinity so due to the increased alkalinity sodium ions enters into the voids or gaps which fills the gap and reduces the swelling. Improper ionization of the cross-linked network may be the reason behind the lower swelling in acidic medium. Major reduction in the swelling capacity of hydrogel in the case of NaCl solution is due to the presence of high ionic concentration in surrounding which decreases the difference in the osmotic pressure between outer and inner phases.

4.6 Characterization

4.6(a) FTIR spectroscopy

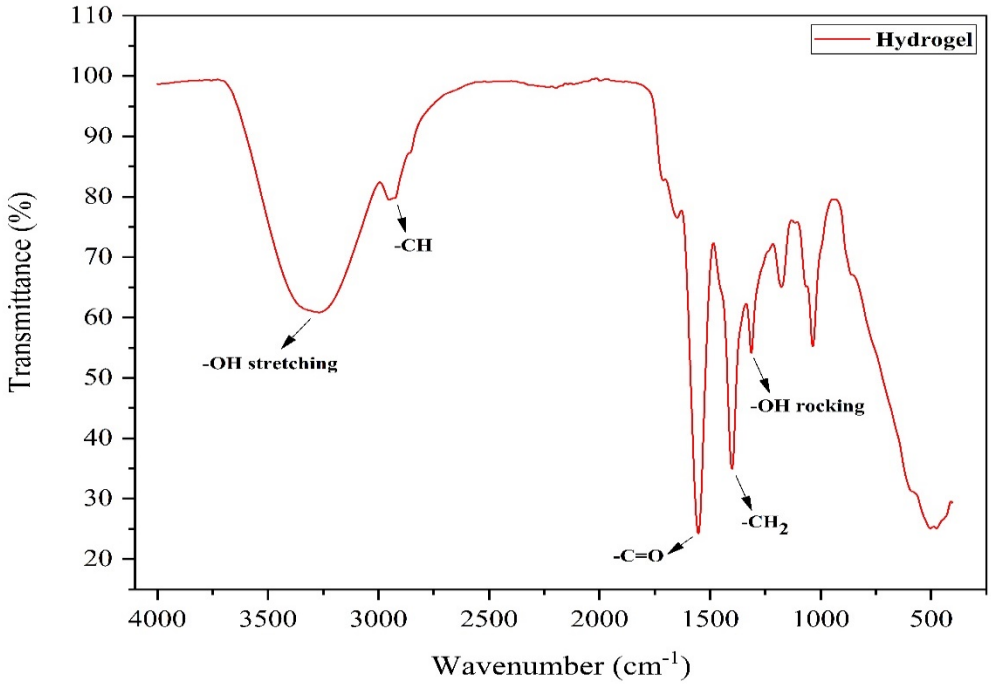

Fig 14 FTIR spectroscopy

FTIR spectra of (CMTKG-PVA) SAH are as shown in Fig.14 CMTKG showed characteristic broad absorption peak at 3428 cm^{-1} for –OH stretching vibrations. The symmetric and asymmetric vibration of $–COO^-$ moiety are assigned to 1415cm^{-1} and 1631cm^{-1}, respectively. In particular, the FTIR spectrum of PVA indicates the broader peak of around 3400 cm-1 for stretching vibration of –OH moieties due to the intra- and extra-molecular hydrogen bonding. Additionally, the peaks at wavenumber of 1720-1737 cm^{-1} , 1440 cm^{-1} , and 1377 cm^{-1} correspond to stretching vibration of –C=O, and bending vibrations of $–CH_2$ and $–CH_3$ groups, respectively.

A broad absorption band at 3332cm^{-1} corresponded to the –OH stretching vibration and $–COO^-$ symmetric and asymmetric vibrations at 1410 cm^{-1} and 1568cm^{-1}, respectively. These peaks correspond to the peaks of CMTKG and PVA (only –OH stretching) This strong transmittance peak at 1568 cm^{-1} was linked with stretching vibration of C=O of the poly- sodium acrylate, whereas the occurrence of bands at 1039 cm^{-1} was characteristic of the CMTKG polysaccharide skeleton. The broad band at 627 cm^{-1} and a peak at 1317 cm^{-1} corresponded to the O=C–N and C–N groups of MBA which proved that the successful cross-linking between CMTKG-PVA-PSA.

4.6(b) Thermogravimetric analysis (TGA)

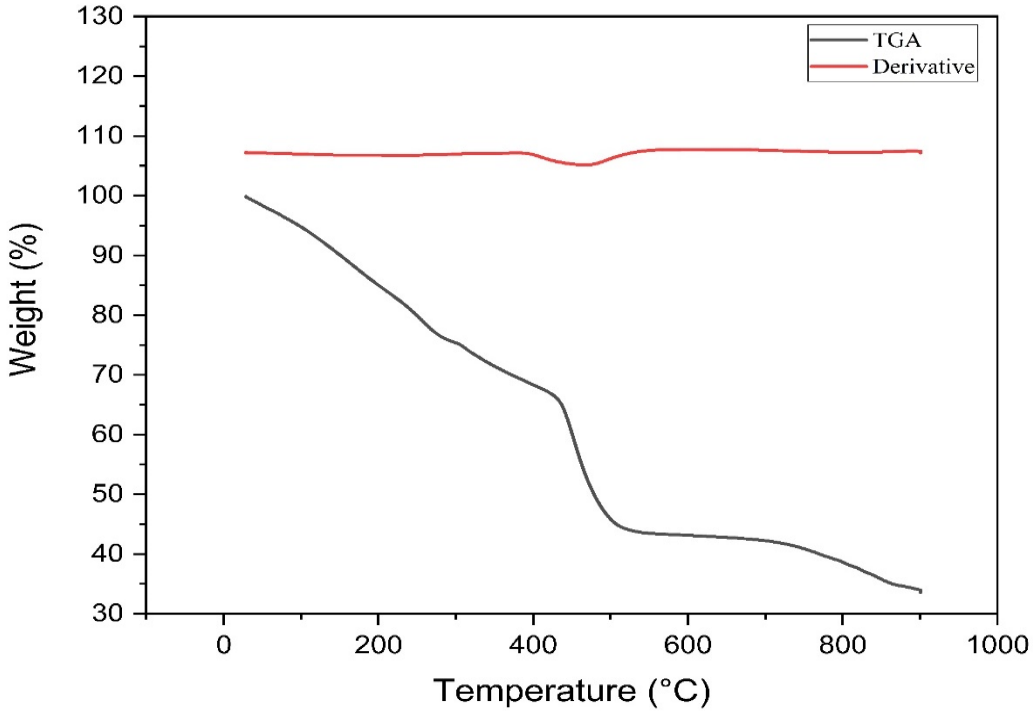

Fig 15 Thermogravimetric analysis (TGA)

For thermal analysis of hydrogel TGA experiment was performed in which sample was taken in small quantity. TGA experiment was started at 25^0C and went upto 900^0C. It is evident from the above graph that from temperature 25^0C to 276.6^0C the amount of weight loss is 22.27%, from temperature 276.6^0C to 428.9^0C the amount of weight loss is around 10.43%, from temperature 428.9^0C to 512^0C weight loss occurred rapidly also a steep downfall in terms of weight of hydrogel can be observed which is around 21.81% in such a small temperature difference, from temperature 512^0C to 900^0C again the amount of weight loss is around 10.87% and hence at 900^0C the amount of residue left as char content is around 33.59% also the rapid decrease in weight in the temperature gap of 428.9^0C to 512^0C is evident from derivative curve which shows that rapid decrease in weight percentage of hydrogel in such a low temperature gap.

4.6(c) Rheological studies

Amplitude sweep

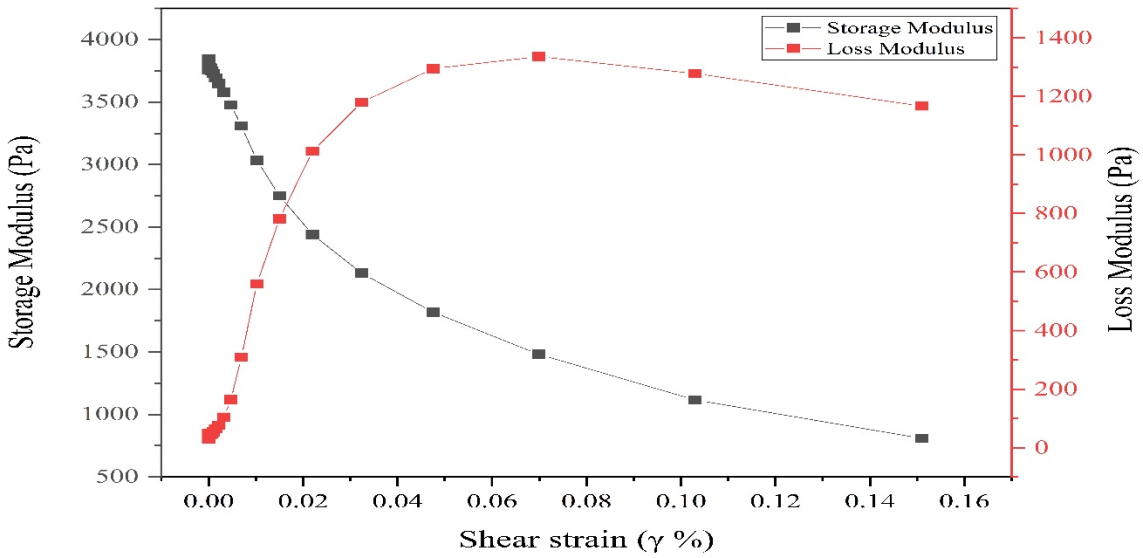

Fig 16 Hydrogel swelled in distilled water

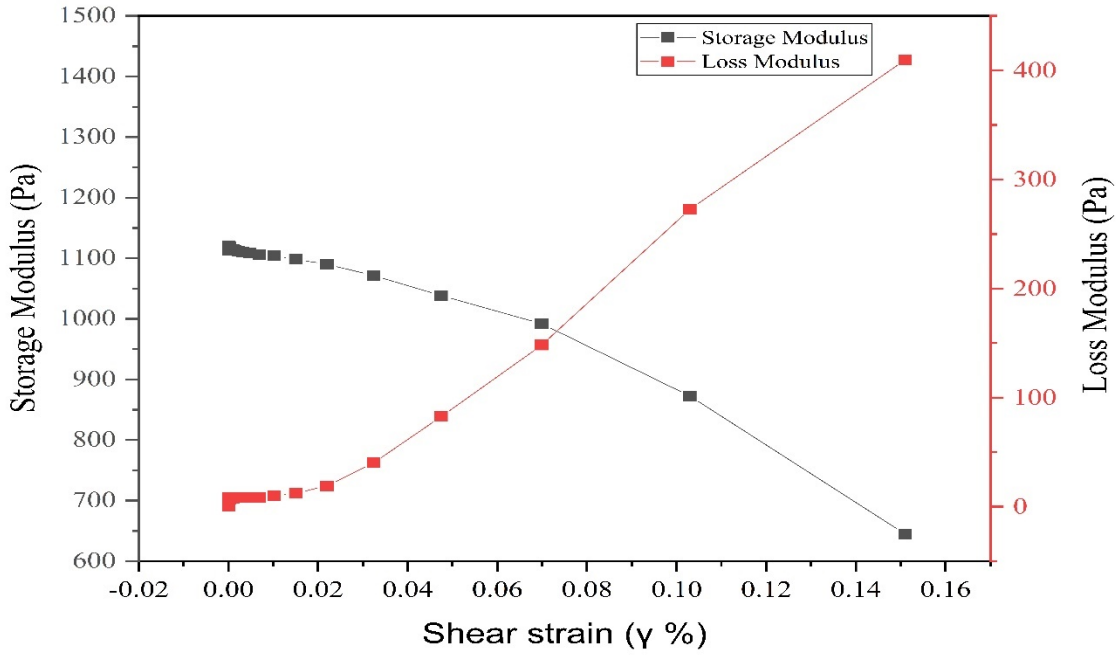

Fig 17 Hydrogel swelled in Saline solution

From the above graph of hydrogel dipped inside distilled water and saline solutions, in both the graphs the value of loss modulus is more or less same whereas the storage modulus for distilled water is high (around 3800 Pa) and for that of saline it is around 1100 Pa which is less in comparison to distilled water due to the presence of ions the chain movement facilitation was reduced resulting in more complexity in structure and less swelling and hance less storage modulus.

For both distilled water and saline as the shear strain increases the storage modulus decreases continuously as on increasing the shear strain the storing capacity of the hydrogel decreases, hydrogel starts losing its stability and loss modulus increases continuously.

Also at low shear strain the rigidity and strength of the hydrogel is high whereas at high shear strain the rigidity and stability of hydrogel is low that may be because of rupture of chains inside hydrogel and also it is evident from result shown in graph that there was steep decrease in storage modulus and steep increase in loss modulus for both saline and distilled water.

Frequency sweep

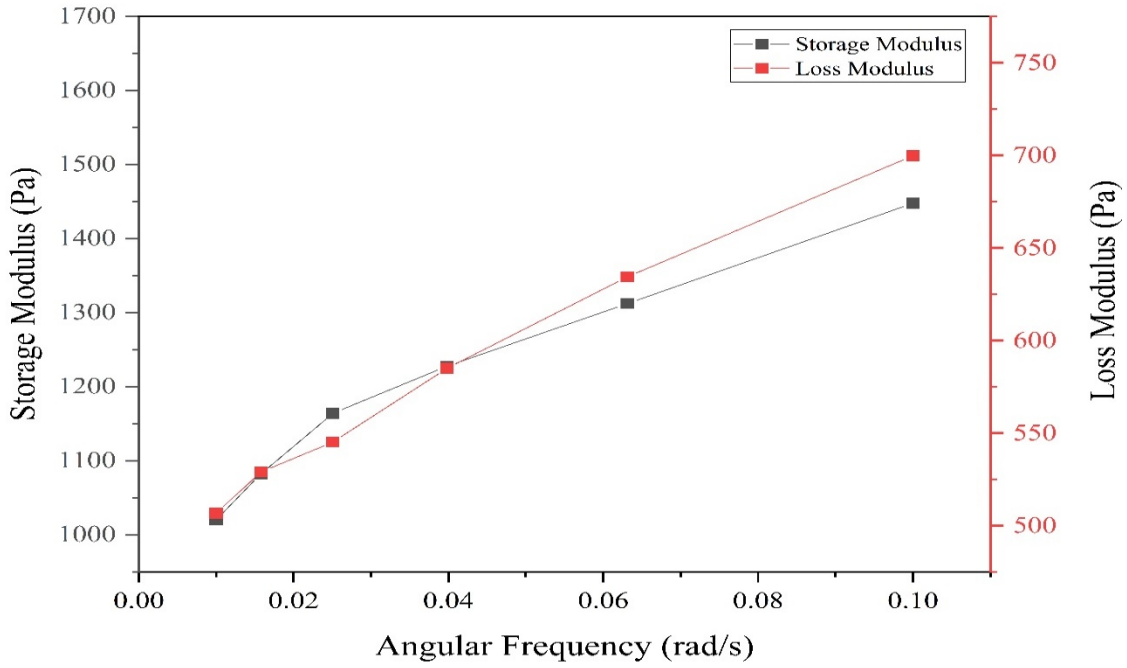

Fig 18 Hydrogel swelled in Distilled water

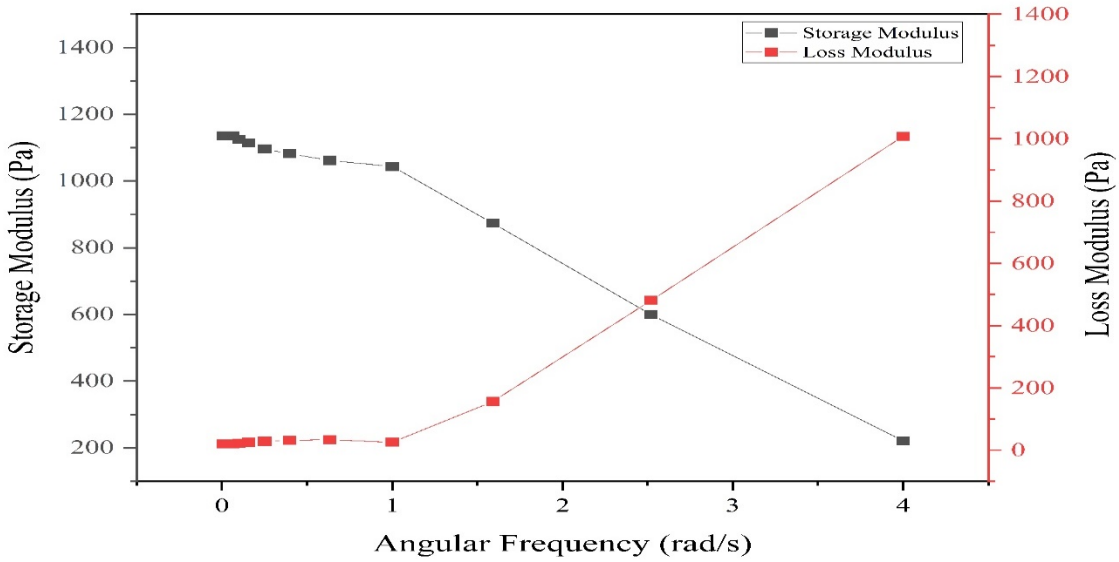

Fig 19 Hydrogel swelled in Saline solution

4.6(d) Scanning electron microscopy (SEM)

SEM images of CMTKG-PVA hydrogel are shown in Fig.20. This analysis showed the morphology of (CMTKG-PVA) hydrogel having spongy surface and interspatial voids. As can be seen from the figures, pores of different sizes can be seen. These pores are the reason for the swelling of hydrogels.

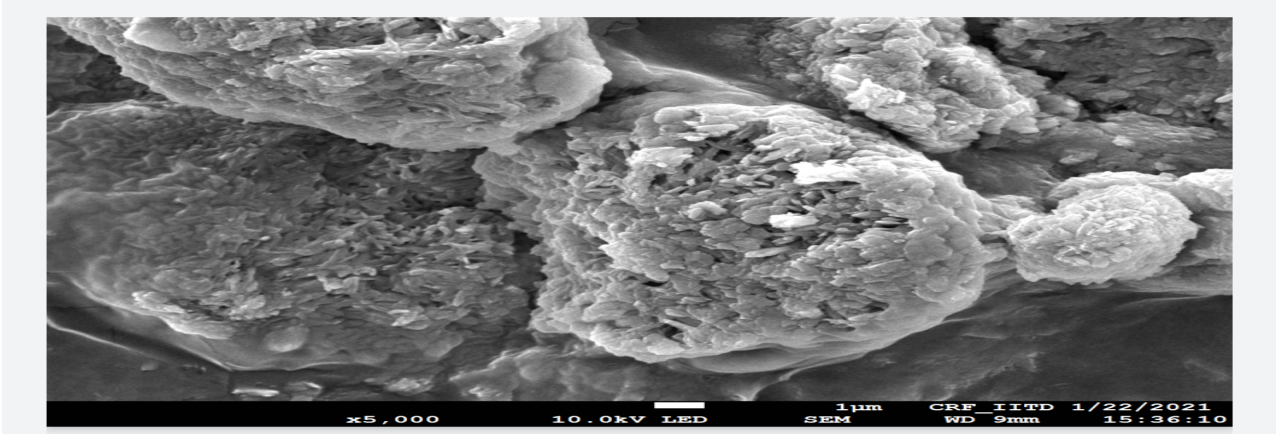

Fig 20 Scanning electron microscopy (a)

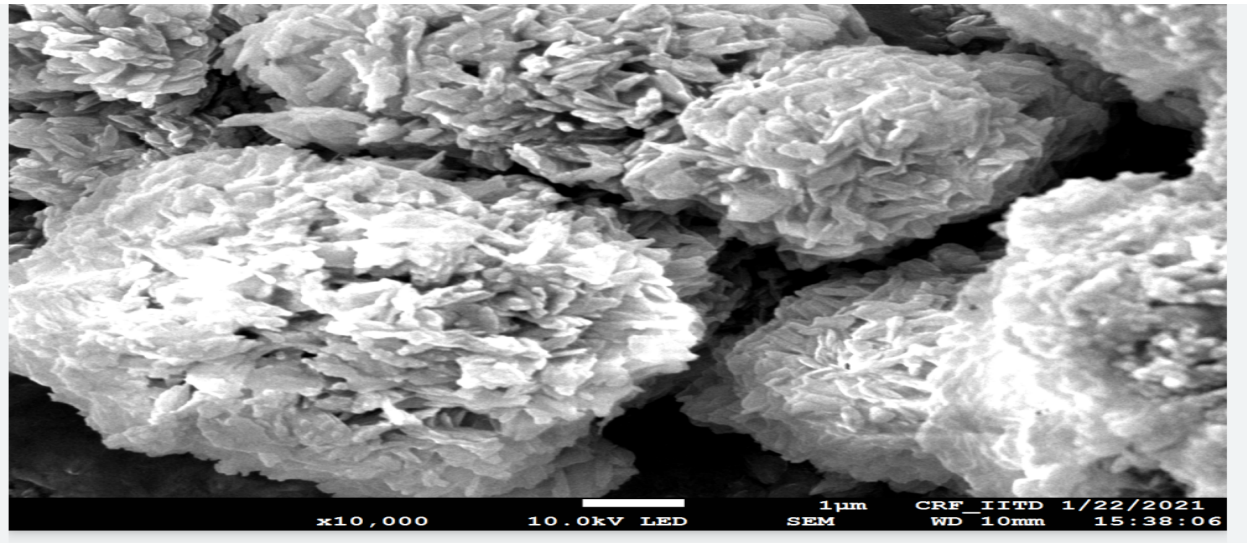

Fig 21 Scanning electron microscopy (b)

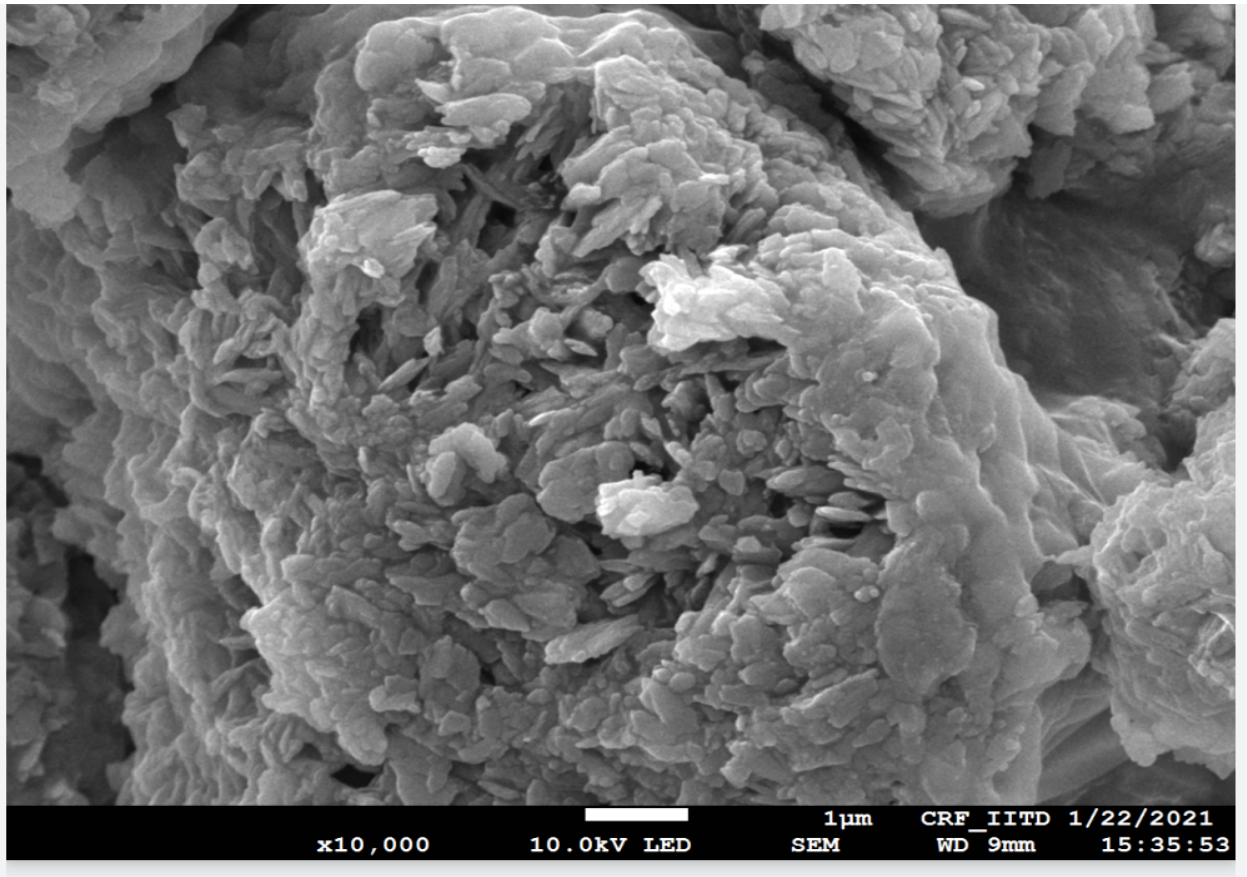

Fig 22 Scanning electron microscopy (c)

Conclusion

In our work a novel combination of CMTKG-PVA was synthesized using different concentrations of CMTKG, PVA, initiator and crosslinker in which a total of 16 samples were synthesized. Then swelling studies were done at 25^0C to observe the swelling behavior of hydrogels then the reaction parameters used in synthesis were optimized using Data Envelopment Analysis along with slack analysis in order to decrease the amount of time, resources and labour which aimed at achieving the goals of Green Chemistry.

Also, the results obtained through DEA analysis were validated by experimental swelling studies and the optimized sample was used for further swelling studies in which the effect of concentration of CMTKG, PVA, initiator and cross linker on swelling studies were explained with the help of graph where it can be concluded that the water absorption would increase as the concentration of CMTKG increased, PVA concentration showed inverse relation with swelling and with the increase in cross linker concentration the stiffness, rigidness of the hydrogel increases and swelling index decreases.

Rheological studies were done in which we compared the results of hydrogels swelled in distilled water and saline solution and we came to know that the storage modulus of distilled water swelled hydrogel is very high as compared to saline swelled hydrogel plus as the shear strain increases the storage modulus of both the hydrogels decreases continuously and loss modulus keep on increasing till complete rupture occurs.

Further characterization tests were performed such as FTIR which showed the composition of hydrogel and validated the presence of polymer. Then Thermo gravimetric analysis was done to check the degradation of hydrogel with change in temperature, hydrogel was able to bear max temperature of 900^0C and at this temperature approx. 33% of the weight was left as char. The structure of hydrogel was studied under Scanning Electron Microscope and voids and gaps were clearly visible at 10,000 magnification.

Applications and Future Prospects:-

In future we will synthesize one more combination with least concentration of MBA and least concentration of PVA as both of them play a major role in swelling of hydrogel and we came to know about their effectiveness via DEA analysis mainly slack analysis. Another thing which I will try to add is to calculate the percentage grafting for every sample and see how it works with DEA in optimizing the reaction variables. Also the hydrogel formed can be easily used for agricultural applications such as

1) As a soil conditioner in order to enhance the supply of water to plants.
2) As a water and macro/micro- nutrient carrier vehicle (controlled release).

Another area of application of this hydrogel is wound dressing, drug delivery, dye removal etc.

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