Swelling of starch – based super absorbents in water, Saline water and effluent water of CEPT

Authors:

1. Shri S.R.Bhatt 2. Prof.R.V.Patel 3. Shri Nimish Shah*

Abstract

Starch graft super absorbents were prepared by graft co polymerization with poly acrylonitrile (PAN). A fundamental relationship exists between the swelling of a polymer in a solvent and the natures of the polymer and the solvent. The swelling properties of this absorbent studies with different type of waters (DM, Tape), saline water (sea water) and effluent collected at different common effluent treatment plant (CEPT) of Ahmedabad. As expected the absorbent shows large variation in swelling capacity with different samples of liquids. We have also studied the performance of this polymer as absorbent on different effluents. As a part of our work we analyzed the polymer for its impact on COD, pH, TDS, TSS, Color of effluent samples. We have studied the effect of different dosage of polymer on its performance with effluents. The work has been carried out as a part of ME dissertation work at ATIRA. For this study, we have taken sample of effluent from three different CEPTs of Ahmedabad: Odhav Green Gujrat Verapi Mahamandal and Odhav Environment Pvt. Ltd.

Swelling at equilibrium has been used extensively to study performance of absorbent with water, saline water and other solvent / liquids, but relatively very little work has been done on obtaining swelling with chemical effluents.

The work has been carried out under dissertation work of M. E. Programme at Ahmedabad Textile Industries Research Association (ATIRA), Ahmedabad. We have carried out this work to access the possibility of application of super absorbent polymer as effluent treatment polymer. The paper will discuss some important practical considerations to improve the water absorbing performance of the polymer produced.

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1. Sr. Deputy Director, Ahmedabad Textile Industry's Research Association(ATIRA), P.O. Ambavadi Vistar, Ahmedabad-380 015
2. Professor, Chemical Engg. Dept. Faculty of Technology & Engineering, M.S.University of Baroda, Kalabhavan, Vadodara- 390 002
3. Lecturer,Chemical Engg. Dept. Institute of Diploma Studies, Nirma University of Science &Technology, Gandhinagar- Srakhej Highway, Post Chandlodia Via Gota, Ahmedabad. Email : nimish_nirma@yahoo.com

***corresponding Author**

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Authors:

1. **Shri S.R.Bhatt** **2. Prof.R.V.Patel** **3. Shri Nimish Shah***

* ***corresponding Author:*** *Lecturer,Chemical Engg. Dept. Institute of Diploma Studies, Nirma University of Science &Technology, Gandhinagar- Srakhej Highway, Post Chandlodia Via Gota, Ahmedabad. Email : nimish_nirma@yahoo.com* ***Work Carried out at*** *Ahmedabad Textile Industry's Research Association(ATIRA), P.O. Ambavadi Vistar, Ahmedabad-380 015*

1. INTRODUCTION:

One of the frontier areas of immense scientific development in the modern times is the environmental field. There is hardly any need to emphasize the fact that the very existence of the mankind is hinged on sustaining natural equilibria, which are threatened by exponentially expanding industrial and commercial activities. Precipitation of various impurities by chemical additives from the industrial and other waste water has been practiced for nearly 6-7 decades in the industrial world and else where, as one of the commercially viable and industrially suitable remedies to water pollution problems. A number of polymeric compounds have been in use for these purposes. They are also used for absorption of water for a number of other purposes like an agriculture, seed coating, fire fighter, storm fighter etc.

Most of these commercially available polymeric gels have serious techno economic limitations such as limited water absorption capacities, toxicity and nonbiodegradability. There fore, an accut need for development of a natural polymeric gel with much higher water absorption capacity, biodegradability in the environment and ecologically friendly disposition in terms of lack of toxicity has always been felt over the years. Extensive literature survey through various search engines as also the literature, scientific journals showed that considerable developmental efforts are underway in these specific areas throughout the world. However the literature survey also indicated that but little work has been carried out towards development of such polymeric gels in India.

The focus of this dissertation as a part, of ME programme under taken by me was obviously development of ingenious, cost-effective and ecofriendly polymeric gels of a newer kind from natural polymers such as starch. Extensive experimental work on selected novel methods to obtain such a polymeric gel from starch carried out in the ATIRA Laboratory as mansion in the various chapters of the dissertation thesis has proved highly successful. The essence of the dissertation is successful development of an innovative polymeric gel of natural origin with exceeding high water absorption capacity, high biodegradability and non-toxic nature. Tentative techno economics aimed at evolving the manufacture of this gel at commercial scale are also encouraging. In addition to its main use as a water absorbing gel, several experimental runs were also carried out to find out the efficacy of the gel for removal of oil from oil-water emulsion and treating the industrial waste waters at Laboratory scale. These innovative usages of the gel proper show a mix bag of results while on the one hand, the newly developed gel has consistently performed for better than the currently available commercial gels in the country in terms of water absorption as testified in thesis, its potential for other applications, on the other hand, remains to be further verified. There is no doubt that further work at pilot plant scale and semi commercial scale using the new gel for a host of objectives such as agricultural, Hygiene products, Membrane Technology, Pharmaceuticals Industry, etc. will go a long way in solving a few of the perennial problems of the mankind.

2. THEORY: SWELLING IN HYDROGELS

2.1 Mechanism Of Swelling In Hydrogels

Hydrogels consist of a polymeric network swollen by an aqueous fluid. The properties of the gel depend on the interaction of these two components. In general, as the specific amount of water absorbed by the hydrogel increases, its permeability to oxygen and water-soluble substances increases, whereas its strength decreases, and the equilibrium hydration becomes more dependent upon variation in the environment.

2.2 Swelling Phenomena

A hydrogel is a three-dimensional network. Although it is incapable of dissolving completely, it absorbs large. For a hydrogel at equilibrium is characteristic of the polymer composition and cross-link density, the temperature, pH, and ionic strength of the medium in which the gel is stored, and the existing hydrostatic pressure. The gel tends to absorb or expel fluid with changes in the environmental conditions, such as the osmotic pressure on the gel.

The osmotic pressure is a function of three distinct components the strength of the polymer-polymer segment interactions compared with the strength of polymer-solvent interactions, the rubber elasticity (qv) of the polymer network, and the hydrogen-ion activity in the aqueous phase (if the polymer chains contain ionizable groups).

Hydrogel polymers have high polymer-polymer segment interactions. Since the segments are predominantly polar, and some segments contain ionic groups, ionic cross-linking, dipole-dipole interactions, and intersegment hydrogen bonding increase intrapolymer attractive forces. However, the polarity of the segments is also responsible for the hydrophilicity of the polymers. Thus, the polymer-solvent interactions are stronger than polymer-polymer interactions. The cohesional forces holding the polymeric chains together are overcome by the solvent, and the polymer segments become surrounded by solvent molecules. The chains expand, and the gel swells. The gels (qv) are complex topological networks. During swelling by absorption of the solvent, the chains between the network junctions distend and assume elongated configurations. This process is limited by the elasticity of the individual polymer chains. If the polymer chains are stretched beyond their equilibration length, the opposing rubber elasticity counteracts the stretching to make the gels collapse, thereby expelling fluid. By analogy, gels that have absorbed less than the equilibrium amount of water tend to expand under the influence of the rubber elasticity and imbibe liquid. Increasing the temperature increase the thermal motion of the segment and aids a collapsed gel to dilate and a swollen gel to contract.

Finally, the effect of the hydrogen-ion activity depends on charge density in the ionic polymeric network. Positive and negative charges are exactly balanced, and the gel as a whole maintains electrical neutrality. Ionizable groups, eg, carboxyls, create a strong localization of charges on the polymer backbone. Counterions in the hydration medium are attracted to the localized charges and reduce the strong electrical repulsion between them by shielding.

The degree of swell can thus be altered by changing the pH or by adding an electrolyte, eg, sodium chloride to the hydration medium. As the concentration of available counterions increases. The effective ionization of the polymer is reduced and the electrostatic free energy of the system decreases. There is a reduction of volume, ie, shrinkage of the gel material.

2.3 Equilibrium Swelling

The amount of water or saline that a hydrogel can incorporate at equilibrium determines the optics, fitting characteristics, and physical properties of the Hyderogels. The degree of saturation with water is a function of the chemical composition of the gel, but also depends on pH temperature, pressure and ionic strength of the hydrating solution.

3. EXPERIMENTAL METHODS

First we manufactured hydrolysed Starch grafted PolyAcrylonitrile by special developed method. Some important steps of that are as below:

- Gelatinization of starch
- Copolymerization of gelatinized starch
- Separation of Graft Copolymers

- Extraction of Homo Polymer
- Saponification of Starch grafted Poly Acrylonitrile (S-PAN)
- Precipitation and separation of Hydrolized SPAN product (HSPAN)
- Characterization of Co polymer

Then we determined Absorbency / Water Retention of the powdered product with DM water. The time duration taken during this work for determine the absorbancy was 24 hrs. We had allow the polymer to swell water for 24hr and then put it to drain unswelled water. After 15-20min. almost unswelled water was drained and then we weight the swollen gel on electronic weight balance. All the reported absorbency are determined is same explained manner.

The aqueous medium we have considered for measuring absorbency, are DM Water, Tap Water, Salt Solution, Sea Water and Effluent of Common Effluent Treatment Plants.

- DM Water: supplied by Ganesh Chemicals, Ahmedabad
- Tap Water: Bore water of ATIRA having TDS: 1578 ppm
- Salt Solution: 0.9% concentrated Sodium Chloride Solution used as salt solution for measurement.
- Sea Water: Sea Water of Arabian Sea collected from Tithal Sea Shore having following compositions

TDS:		44,346 ppm
SALTS:	Sodium:	9000 ppm
	Potassium:	3600 ppm
	Magnesium	974.6 ppm
	Calcium	292.6 ppm

- Effluents: The effluent samples of three different CETPs were used.
  - Gujarat Vepari Mahamandal (GVM), Vatva, Ahmedabad
  - Odhav Environment Pvt. Ltd. (OEPL) , Vatva, Ahmedabad
  - Odhav Green (OG) , Vatva, Ahmedabad

With the collected samples of different CETPs we had carried out following tests with universally used standard established methods.

Total Solid (TS)

Principle: Total solids are determined as the residue left after evaporation of the unfiltered sample.

Total Dissolved Solids (TDS)

Principle: Total dissolved solids are determined as the residue left after evaporation of the filtered sample.

Total Suspended Solids (TSS)

Determine total suspended solids as the difference between the total solids and total dissolved solids. TSS = TS – TDS

Chemical Oxygen Demand (COD)

Chemical oxygen demand is the oxygen required by the organic substances in water to oxidize them by a strong chemical oxidant. The COD usually refers to the laboratory dichromate oxidation procedure.

COLOUR : Spectrophotometric Method

Principle: The Colour of a filtered samples expressed in terms that describe the sensation realized when viewing the sample. The hue (red, green, yellow, etc.) is designed by this term “dominant wavelength” the degree of brightness by “luminance” and the saturation (pale, pastes, etc.)by “purity”. These values are best determined from the light transmission characteristics of the filtered sample by means of a spectrophotometer.

Spectrophotometer: Having 10 mm absorption cell, a narrow (10 – nm or less) spectral band, and an effective operating range from 400 – 700nm.

pH (Potentia hydrogenii)

Principle: pH is the negative $\log_{10}$ of the hydrogen ion concentration in a solution. It can be measure by colorimetric methods using various indicators or paper strips. However the use of colorimetric methods are less convenient and less accurate. For accurate measurement of pH,

4. RESULT AND DISCUSSION

Table: 1. Absorbency Measurement

Batch No.	DM Water	Tap Water	Salt Solution	Sea Water	Effluent		
					GVM	**OE**	**OG**
1	45.20	-	-	-	-	-	-
2	23.70	-	-	-	-	-	-
3	156.70	-	-	-	-	-	-
4a	518.13	-	-	-	-	-	-
4b	278.97	-	-	-	-	-	-
5a	760.16	-	41.68	-	-	-	-
5b	640.71	81.54	30.44	-	-	-	-
6a	406.75	57.51	20.15	-	-	-	-
6b	331.43	53.55	19.44	-	-	-	-
7	271.91	55.53	21.26	-	-	-	-
8	767.45	78.74	31.20	-	-	-	-
9	308.00	77.68	46.11	-	-	-	-
10	1734.60	144.80	57.59	42.2	58.76	88.8	47
11	636.28	69.61	30.32	-	-	-	-
12	821.80	106.30	56.05	55.1	-	-	-
13	847.90	132.85	49.80	38.1	-	-	-
14	829.45	159.35	59.20	54.2	-	-	-
15	801.95	89.60	37.25	39.7	-	-	-
16	839.45	115.10	45.10	40.9	-	-	-

Absorbency varies with monomer, solvent, order of process steps like neutralization, precipitation, etc. Absorbency lowers then DM Water due to salts present in tap water. Internationally the absorbency measured with DM water and salt solution of 9% NaCl .It is always found lower due to presence of salt. When heavy metals are present in media, the repeatability of result reduces. The absorbed material showed suspended particles absorbed with water.

- **Performance of Polymer with effluents**

  The performance of polymer product is tested with batch no.10 only

Table 2 Performance of Polymer with GVM effluents

PPM	COD	TSS	TDS	Colour	PH	Absorbency
0	1723	152	5792	1.31	6.97	0

50	1440	150	6300	1.472	8.08	20
100	1200	130	6578	1.39	8.15	62
150	1144	110	6366			
200	1192	66	6766			

Table 3 Performance of Polymer with OE effluents

PPM	COD	TSS	TDS	Colour	pH	Absorbency
0	1560	196	11322	1.07	7.77	0
50	1424	212	11472	1.64	8.13	56
100	1220	214	12430	1.83	8.13	115
150	1072	118	12692			
200	1144	66	12842			

Table 4 Performance of Polymer with OG effluents

PPM	COD	TSS	TDS	Colour	pH	Absorbency
0	760	100	3300	0.613	7.56	0
50	1040	102	4220	0.491	8.25	47
100	1067	200	6824	0.486	8.24	2
150	1040	60	3870			
200	1176	144	3762			

CONCLUSION:

The present work includes the preparation, modification, characterization and testing the performance of Hydrolyzed starch grafted Poly Acrylonitrile (HSPAN) super absorbents.
The absorbency of the material is due to swelling phenomena and hydrophilic nature. The water swells in the polymer increase its total volume and it looks like gelly. This water absorbing property is due to the ionic components present in the polymer. The hydrolyzed starch grafted Polyacrylonitrile (HSPAN) is the product we have prepared during our work. The continuous improvement in water absorbing results are found.

The performance of polymer with effluents were tested. Here it shows that with 150 ppm, we can get reduction in COD of GVM effluent upto 34%. Same amount with OEPL effluent shows reduction of 31.28%. but with OG effluent, the behaviour is just opposite. It shows increase in effluent COD after treatment with the polymer. With TSS, the polymer shows that increase in dosage reduces TSS in all effluents after treatment with polymer. The results of analysis shows that the behavior of polymer is found varying with TDS of treated effluents. As all three effluents are of three different CETPs, and all of them are having different characteristics, so the results may showing such variation.

Herewith we had tried to use this newly developed product in the combat with environmental problems. At this stage, further work is required to conclude any particular statement. Further work in this direction may develop new vision and techniques, which may lead us to some favourable results.