GLYCEROL AND CITRIC ACID BASED BIODEGRADIBAL NOVEL POLYMERS

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ABSTRACT

Polymers based on glycerol and citric acids have been synthesized. These polymers are found to be biodegradable in nature and may be used as surfactants. Polymers were synthesized using required amount of glycerol and citric acid in addition with small quantity of ingredients namely polyethylene glycol(400), sorbitol, sodium bisulphate and sodium bisulphite. The synthesized polymers have been analyzed for physicochemical characteristics like % solids, pH, H.L.B ratio and % oxirane oxygen value. In addition to physiochemical analysis selected polymer was analyzed for its biodegradability. The result shows that the polymer is biodegradable and suitable ingredient for preparation of biodegradable surfactant.

Keyword : - *Glycerol, Polyethylene glycol(400), Citric acid, Surfactants, Biodegradability, Polymer.*

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1. INTRODUCTION

The ever increasing uses of non biodegradable surfactants are causing major concern in water polution. The surfactants used in powder, liquid detergents and cleansing preparations are mainly based on petroleum byproduct. These surfactants are refractory in nature, so they cause pollution and damage the ecosystem.
To avoid this problem we synthesized polymers mainly based on glycerol and citric acid.
Glycerol [1] and citric acid [2] are vegetable origin by products. Polymers which are biodegradable, contains ether, ester and carboxylic acid groups in their structure. These groups also help to make polymer as good surfactant and the cleansing preparations made from these polymers are ecofriendly in nature. For the synthesis of novel polymers we used small quantity of polyethylene glycol (400), sorbitol, sodium bisulphate, sodium bisulphite with glycerol and citric acid as major ingredients. Synthesized polymers were analyzed for various physicochemical properties like% solids, pH, viscosity, H.L.B ratio and % oxirane oxygen value by standard laboratory methods [3-8]. The selected polymer was analyzed for biodegradability test on the basis of physiochemical properties.

2. MATERIAL AND METHODS

2.1. REACTION PROGRAMMING AND STEPS IN SYNTHESIS OF POLYMERS

Polymers of various compositions were prepared in batch process. The mole ratios, reaction temperature and addition of ingredients are detailed below in four steps:-

Step 1:- Glycerol, Citric acid, Polyethylene glycol (400), Sorbitol, Sodium bisulphate and Sodium bisulphite were added and converted into a homogenous dispersion by using electrically controlled homogenizer. The dispersion should have flow and mobility. The dispersion was introduced into the reactor (as given Table.1).
Step 2:- The mass is slowly heated to 80^0C in about 15 minutes. The reaction was then taken to the desired temperature of.120^0-130^0C in about 20 minutes. The charge was monitored every fifteen minutes for flow, homogeneity and viscosity.
Step 3:- After attending the desired viscosity and celerity the heating was stopped and mass cooled to 80^0C.
Step 4:-The batch was withdrawn, filtered through a strainer and stored in tightly closed bottles. The polymer sample was tested for Physiochemical analysis by standard laboratory methods.

3. BIODEGRADABILITY ANALYSIS OF SELECTED POLYMER

Experimentally the biodegradability of polymer was analyzed using waste water treatment method. For this, ratio of Biochemical Oxygen demand (BOD) and Chemical Oxygen Demand (COD) was analyzed.

3.1. Chemical Oxygen Demand (COD)[9]:

The Chemical Oxygen Demand (COD) test measures the oxygen required to oxidize organic matter in water and wastewater samples by the action of strong oxidizing agents under acidic conditions.

Procedure: Place 0.4g $HgSO_4$ in a reflux flask. Add 20 ml or an aliquot of sample diluted to 20 ml with distilled water. Mix well, so that chlorides are converted into poorly ionized mercuric chloride. Add 10 ml standard $K_2Cr_20_7$ solution and then add slowly 30 ml H_2SO_4which already contains silver sulphate. Mix well, if the colour turns green, take fresh sample with smaller aliquot. Connect the reflux flask to condenser and reflux for 2 hrs at 150^0C. Cool and wash down the condensers with 60 ml distilled water. Cool and titrate against standard ferrous ammonium sulphate using ferroin as indicator.
Near the end of the titration colour changes sharply from green blue to wine red.

Calculation:

COD as mg /L= (B-S) X N X 8000/V

Where:

B = Ferrous ammonium sulphate used for blank (ml)
S = Ferrous ammonium sulphate used for sample (ml)
N =Normality of Ferrous ammonium sulphate
V =Volume of sample taken (ml)

3.2. Biochemical Oxygen demand (BOD) [10, 11]:

The biochemical oxygen demand (BOD) test is based on mainly bio-assay procedure which measures the dissolved oxygen consumed by micro-organisms while assimilating and oxidizing the organic matter under aerobic conditions. The standard test condition includes incubating the sample in an air tight bottle, in dark at a specified temperature for specific time.

Procedure of BOD Analysis:

1. Preparation of Dilution Water:

The required volume of distilled water was aerated in a container by bubbling compressed air for 8 to 12 hours to attained dissolved oxygen saturation level.
It was allowed to stabilize for 4 hours at room temperature. At the time of use, 1 ml each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride were added for each liter of dilution water.
5 ml of treated sewage per liter of dilution water was added for seeding purpose.

2. Dilution of Sample and Incubation:

The sample was neutralized to pH 7.0 using alkali.

3. Pre –treatment Methods:

- Samples were thoroughly shaken just before dilutions were made. We made series of dilutions for a sample such that at least three of the dilutions should depleted 20 % to 90 % of initial dissolved oxygen. The C.O.D. value was treated as guideline for the purpose of dilution.
- Carefully transferred the prepared dilution water into one liter graduated cylinder until it was half full, without any air entrapment. Then added appropriate quantity of sample into the cylinder without producing any air bubbles. The volume was made up using dilution water. Mixed well with glass rod without any air entrapment. Filled the two BOD bottles carefully without any air bubbles inside it. Stopper the bottles and prepared the other dilution of sample in similar manner.
- Also the standard dilution water was taken into BOD bottle and stopper them after filling them completely.
- Utilized one set of entire series of dilution prepared above for immediate determination of dissolved oxygen and kept the other set in a BOD incubator maintained at 20ºC(±0.1^0C) for 1, 2, 3..........10

days or alternative days. After 1st day to 10th day we determined the dissolved oxygen concentration of all the incubated sample of the set.

4. Determination of Dissolved Oxygen [12]:

The sample was collected in 125ml BOD bottle, 2 ml of manganese sulphate solution followed by 2 ml of alkaline iodide and sodium azide solution were added. The contents were mixed thoroughly by shaking the bottle several times by placing thumb over it. The precipitate was allowed to settle at the bottom. After settling 2 ml of concentrated sulphuric acid was added to dissolve the precipitate. Again it is mixed and shacked to dissolve liberated iodine. This solution was taken and titrated immediately against standard sodium thiosulphate solution by adding 3-4 drops of starch indicator solution. The end point was pale blue to colorless. The dissolved oxygen in mg/L is equal to the volume in ml of the standard thiosulphate solution used for titration.

Formula for calculate the BOD:

BOD mg/L = $(D_0 - D_1)$-(B) X Volume of the diluted sample (ml)/V(ml)

Where,

D_0 = Dissolved oxygen in sample on 0 day

D_1 = Dissolved oxygen in sample on $1^{st}/2^{nd}$/---- 10^{th} day

B = $(C_0 - C_1)$

C_0 = Dissolved oxygen in blank on 0 day

C_1 = Dissolved oxygen in blank on $1^{st}/2^{nd}$/--- 10^{th} day

V = Volume of sample taken (ml)

TABLE-1: COMPOSITION OF NOVEL POLYMERS

Sr.No.	Polymer (Ingredients in %)	S19	S26
1	Glycerol	75	45
2	Polyethylene Glycol (400)	5	20
3	Sorbitol	10	10
4	Citric acid	5	20
5	$NaHSO_4$	2.5	2.5
6	$NaHSO_3$	2.5	2.5

TABLE- 2: PHYSICOCHEMICAL ANALYSIS OF NOVEL POLYMERS

Sr.No.	Polymer Properties	S19	S26
1	% Solids	90.40	89.90
2	pH(1% solution)by Digital pH meter	4.28	3.37
3	Viscosity In Seconds (ford cup no4. At 30^0C)	200	220
4	H.L.B Ratio	17.6	16.29
5	% Oxirane oxygen (By HBr method)	3.7	4.57

4. BIODEGRADABILITY ANALYSIS OF POLYMER S26:

4.1. Observations for chemical oxygen demand for polymer S26

a) Ferrous ammonium sulphate (FAS) used for blank (B) = 6.8ml
b) Ferrous ammonium sulphate (FAS) used for sample(S) = 5.8ml
c) Normality of Ferrous ammonium sulphate (FAS) (N) = 0.1N
d) Volume of sample taken (V) = 2 ml

Calculation: COD as mg /L = (B-S) X N X 8000/V

$$\text{COD as mg /L} = \frac{(6.8-5.8) \times 0.1 \times 8000}{2}$$

COD as mg /L = 400.00 mg/L

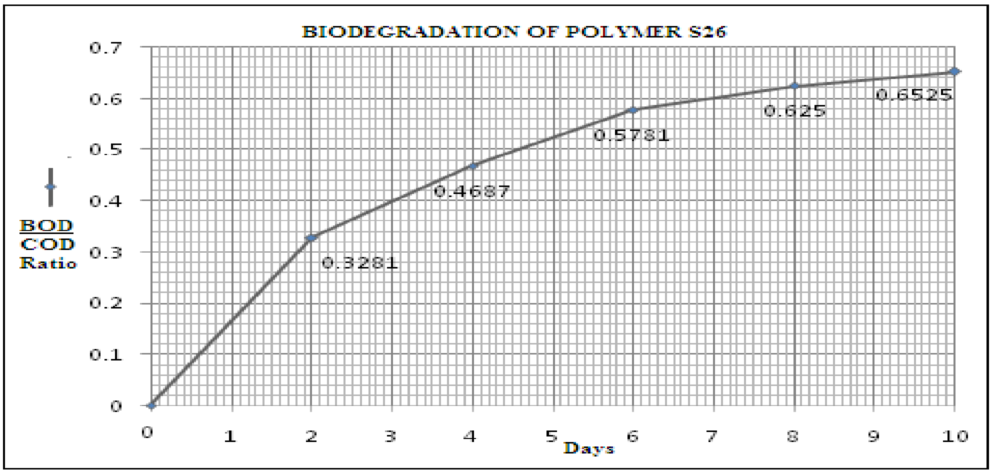
TABLE – 3: OBSERVATIONS FOR DISSOLVED OXYGEN FOR POLYMER S26

Day	Trial no	Sample volume (ml).	Volume of $Na_2S_2O_3$ used(ml)	Dissolved Oxygen (mg/L)
0 Day	Blank	125	6.2	6.2
	Polymer S26	125	5.1	5.1
2nd Day	Blank	125	6.1	6.1
	Polymer S26	125	2.9	2.9
4th Day	Blank	125	6.1	6.1
	Polymer S26	125	2.0	2.0
6th Day	Blank	125	6.0	6.0
	Polymer S26	125	1.2	1.2
8th Day	Blank	125	6.0	6.0
	Polymer S26	125	0.9	0.9
10th Day	Blank	125	6.0	6.0
	Polymer S26	125	0.7	0.7

TABLE-4: ANALYSIS OF BIODEGRADABILITY OF POLYMER S26

Sr.No	Days	Biochemical Oxygen demand (BOD) mg/lit	Chemical Oxygen Demand (COD) mg/L	BOD/COD Ratio
1	2nd Day	131.25	400.00 mg/L	0.3281
2	4th Day	187.50		0.4687
3	6th Day	231.25		0.5781
4	8th Day	250.00		0.6250
5	10th Day	262.50		0.6525

CHART -1: RATE OF BIODEGRADABILITY ANALYSIS OF POLYMER S26



5. RESULTS AND DISCUSSION

1. The composition of various polymers based mainly on glycerol and citric acid are given in Table 1. Polyols like glycerol, polyethylene glycol (400) and sorbitol were reacted with citric acid, sodium bisulphate and sodium bisulphite to form polymer. Sodium bisulphate and sodium bisulphite help to increase the rate of reaction.
2. The Physicochemical analysis of various polymers is given in Table 2. 89.9 to 90.40 % solids are present in both compositions. Samples have pH range of 3.3 to 4.28 (1%consentrated solution of polymers was used for analysis). All samples have excellent viscosity range 200 to 220 seconds. Polymers have H.L.B ratio between rang 16.29 to 17.6 and % oxirane oxygen value rang 3.7 to 4.57.
3. On the basis of physiochemical analysis of polymers we select S26 polymer for biodegradability analysis.
4. Chemical oxygen demand of diluted polymer S26 was observed to be 400 mg/L.
5. Analysis of Biochemical oxygen demand was given in Table 3. Similarly biochemical oxygen demands by chemical oxygen demand ratio were given in Table 4. From this ratio it is clear that polymer S26 biodegraded to be extend of 60% within 8 days.
6. Biodegradability analysis of polymer S26 is given in Chart 1.

6. CONCLUSIONS

Polymers based on glycerol and citric acid are given in Table-1. In polymer S19, 75 % glycerol has been used with 5% citric acid. Similarly in polymer S26, 45% glycerol has been used with 20% citric acid. Physiochemical analysis of novel polymers shows that polymers have good viscosity range 200 to 220 seconds with good % solids, which may help to easily incorporate polymers in any cleansing preparations.
H.L.B ratio indicates that they must be used as ingredients of cleaning material like surfactants. From % oxirane oxygen value suggests that the novel polymers may contain ether or ester linkage in their polymeric structure shown in Table 2.
In Table- 4, Biochemical oxygen demand to chemical oxygen demand ratio of polymer S26 is given, from this ratio we conclude that the BOD/COD ratio 0.6 was reached after 8th day..It means that polymer degraded 60% within 8 days. Chart 1 depicts the biodegradability profile of polymer S26. Thus from these results and analysis it can be concluded that the polymer S26 is biodegradable in nature and hence may be used for replacement of petroleum based surfactants used in cleansing preparations to formulate biodegradable surfactant products.

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