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Synthesis, Characterization and Utilization of Starch Hydroxypropyl Sulphate for Cationic Dye Removal

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Abstract

The best conditions for synthesis of starch hydroxypropyl sulphate as per the dry method were firstly established. This was done through a thorough investigation into factors affecting the synthesis including concentrations of both the NaOH catalyst and the 2-hydroxy-3-chloropropyl sulphate along with duration and temperature of the reaction. The resultant newly synthesized 2-hydroxy-3-chloropropyl sulphate was then reacted with starch to obtain starch hydroxypropyl sulphate ultimately. After being characterized by making use of IR spectroscopy analysis and scanning electronic microscope, the starch hydroxypropyl sulphate samples were submitted to evaluation for cationic dye removal using Methylene Blue (MB). Cationic dye removal was studied under a variety of conditions. Factors involved encompass initial dye concentration, duration, sulphur %, pH and adsorbent dose. 100% dye removal could be achieved under certain conditions which were described in the text.

Keywords

1. Introduction

Wastewater treatment is a major problem around the world. Growing along with the population growth, industries create environmental problems and health hazards for the population. Hence, environmental concerns behoove scientists and engineers to develop materials and methods to lower the extent of pollution of the environment [1].

In modern industrial society, dyes are widely used to color products for textiles, food, printing and dyeing. So

they are an integral part of many industrial effluents, they are highly visible and can have undesired effects not only on the environment, but also on living creatures. Because the degradation products of some dyes may be carcinogenic and toxic, they are considered as an important source of water pollution and their treatment becomes a major problem for environmental managers.

The release of colored wastewater from these industries effluent may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain. There are various conventional methods of removing dyes from waters.

Adsorption is one of the most efficient methods to remove pollutants from wastewater because of its low cost and ease of operation. Many studies have been made on the possibility of using adsorbents based on clay minerals [2]-[4], activated carbon [5], fly ash [6] [7], weeds [8], crosslinked amphoteric starch [9], Indian rosewood sawdust [10], and crosslinked chitosan beads [11].

However, the adsorption capacity of these adsorbents is not very large, so new absorbents are still under development to improve adsorption performance.

Starch and its derivatives represent a cheap and environmentally safe source of raw material for the reparation of low-cost adsorbents that may be useful for the removal of pollutants from wastewater. Because of its particular characteristics (renewable, abundant and biodegradable raw resource) and properties such as its high reactivity and chemical stability, resulting from the presence of chemically reactive hydroxyl groups in its polymer chains [12], making it possible to chemical modify starch according to different requirements, this biopolymer represents an interesting alternative as an adsorbent. After modification, starches have suitable expansion, huge pore volume and high specific area, which can enhance its adsorption ability. It means that modified starches are more suitable as adsorbent for dyes and heavy metals or as catalyst carrier materials. Therefore, the preparation of, renewable, nontoxic, low cost ionized starch is not only of importance in the field of modern pharmacy but also has great prospects in the water treatment field.
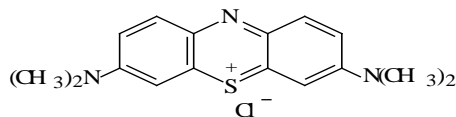
In recent years, many research works have covered the preparation of neutral starch and their physicochemical properties [13]. Common neutral starch mainly adsorb physically, so its adsorption and selectively adsorption ability are weak. Ionization of starch can improve its adsorption ability by enhancing the active groups. Anionic starches have high affinity to positively charged drugs, dyes, metals ion [14], thus enhancing the selective adsorption performance by introducing the carboxylate [15]. The carboxylation has been done via saponification of poly (acrlyamide)-starch graft copolymer, or poly(acrylonitrile)-starch graft copolymer, or poly (methylacrylate)-starch graft copolymer, graft polymerization of starch with methacrylic, or acrylic acid [16].

Among polymers of renewable resources; starch and its derivatives such as sulfonic starch [17]-[19] was currently enjoying increased attention. Starch sulfonation could be carried by using starch, dichloroethane and chlorosulphonic acid [20]. Starch sulfate was one of the modified starches which have biological activities. It was reported that starch sulfate had also the activity of anti-HIV, anti-tumour and antivirus. The starch sulfate was a good inhibitor to pepsin. The starch sulfate prepared had a potential application for the medical uses. Potato starch sulfate was obtained by the reaction between potato starch and chlorosulfonic acid in pyridine [21].

Using the mixture of concentrated sulfuric acid and n-propanol as sulphonating agent, the starch sulfate was prepared with degree of substitution 0.1 - 0.6 [22]. Potato starch sulphate was synthesized by the reaction between potato starch and sulphuric acid in ethanol [23].

Methylene Blue (MB) **Scheme 1**, is selected as a model compound for evaluating the waste to remove cationic dye from wastewaters. MB is a thiazine (cationic) dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on. Although MB is not considered to be a toxic dye, it can reveal harmful effects on living things.

Current work is undertaken with a view to synthesize, characterize and use green starch-based materials, namely starch hydroxypropyl sulfate, which are capable of cationic dye removal from aqueous solutions. To achieve the goal, thorough investigations into factors affecting the synthesis of these green starch derivatives, as well as, affecting removal of the cationic dye upon utilization of these newly synthesized green materials. Variables studied in the synthesis comprise concentrations of both the catalyst and the 2-hydroxy-3-chloropropyl sulphate as well as duration and temperature. Meanwhile variables of the utilization in dye removal include concentration of the initial dye, duration, sulphur %, pH, molar mass and adsorbent dose. Methylene blue (MB) is the dye used. The morphology of starch hydroxypropyl sulfate is examined using Scanning Electron Microscopy (SEM) whereas Fourier Transform InfraRed spectroscopy (FTIR) is used for determination of the newly introduced groups in the microstructural organization of starch.

Scheme 1. Structural of methylene blue (MB) dye.

2. Experimental

2.1. Materials

Maize starch was supplied by Cairo Company for Starch and Glucose. Methylen Blue (MB), in commercial purity, were purchased from Aldrich Chemical (Germany), and used without further purification. Sodium bisulphite, hydrochloric acid, sodium hydroxide, epichlorohydrin and ethanol were of analytical grade chemicals.

2.2. Preparation of 2-Hydroxy-3-Chloropropyl Sulphate

This compound was prepared via reacting 0.9 mole of sodium bisulphate with 1 mole epichlorohydrin, until one phase under reflux was formed. After cooling to 60°C - 70°C reaction product was poured into an excess of 96% ethanol. Thus prepared compound was filtered and dried.

Complete transformation of sulphite to sulphate group was effected by oxidizing the product under heating using a ventilating oven.

2.3. Preparation of Starch Hydroxypropyl Sulphate

The starches hydroxypropyl sulphate was prepared by reacting starch with 2-hydroxy-3-chloropropyl sulphate, in presence of sodium hydroxide using the dry state technique according to a previous method [16].

2.4. Preparation of Cationic Dye Solution

The dye stock solutions were prepared by dissolving dyes in distilled water to 500 mg/L. The experimental solutions were obtained by diluting the dye stock solutions in proportions to different initial concentrations

2.5. Dye Sorption

Adsorption experiments were carried out in a rotary shaker at 150 rpm using 250 mL-shaking flasks containing 50 mL of dye solutions at different concentrations and initial pH values of dye solutions. The initial pH values of the solutions were previously adjusted with 0.1 M HCl or 0.1 M NaOH using a **DEEP VERSION** model (EI) pH meter. The adsorbent (g) was added to each flask, and then the flasks were sealed up to prevent any change of volume of the solution during the experiments. After shaking the flasks for a predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the adsorbent by filtration.

The pH values of the separated dye solutions were again measured and changes in pH values were recorded. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dye with a Shimadzu ultraviolet visspestrophotometer (Japan).

The dye sorption value (m mol/100g sample) of the treated sample was calculated. The sorption value was calculated using the following equation:

Dye sorption value (m mol dye /100 g sample) = Dye sorption value of starch hydroxypropyl sulphate − Dye sorption value of native starch.

% of dye removal = (Dye sorption value (m mol dye/100g sample)/Initial dye concentratin (m mol dye/100g sample) × 100.

2.6. Testing and Analysis

- The sulphite and sulphate contents were determined according to reported methods [24].
- The chlorine content was determined according to reported method [25].
- FTIR spectroscopy.
  The FTIR spectra were obtained from KBr pellets of native and modified starch samples using FTIR spectro-

photometer (JASCOFT/IR-6300, Japan) in the range of 400 - 4000 cm^{-1}.
- Scanning electron microscopy.

By using a scanning electron probe microanalyzer (JXA-840A) JEOL, Tokyo Japan, mages of scanning electron microscopy were studied. The specimens in the form of films were mounted on the specimen stabs and coated with thin film of gold by the sputtering method. The micrographs were taken at magnification of 1000 using 10 kV accelerating voltage.

3. Results and Discussion

3.1. Synthesis of Starch-2-Hydroxypropyl Sulphate

3.1.1. Sodium Hydroxide Concentration
The dependence of the extent of the reaction of starch with 2-hydroxy-3-chloropropyl sulphate (expressed as sulpher %) on the NaOH concentration is shown by **Figure 1(a)**. The reaction was carried out for 180 min at 80˚C, using starch (25 m mole), 2-hydroxy-3-chloropropyl sulphate: starch molar ratio 0.5:1, and different sodium hydroxide: 2-hydroxy-3-chloropropyl sulphate molar ratios (3.13 - 25).

It is seen (**Figure 1(a)**) that, increasing sodium hydroxide concentration based on 25 m mole of 2-hydroxy-3-chloropropyl sulphate upto 18.75 m mole/L enhances significantly the extent of the reaction. Further increase in sodium hydroxide concentration has, indeed, a negative impact on the extent of the reaction, expressed as sulphur percent. The enhancement in the extent of the reaction by increasing sodium hydroxide concentration is rather logical and implies that lower sodium hydroxide concentrations are not sufficient enough to drive the reaction to its maximum. Once the latter is attained higher sodium hydroxide concentrations act in favor of alkaline hydrolysis of the functional group (Equation (3)) of 2-hydroxy-3-chloropropyl sulphate and/or splitting off of the 2-hydroxy-3-chloropropyl sulphate moieties from the starch via alkaline hydrolysis of the chemical bonds linking the starch molecules with these moieties (Equation (4)). Thus, it can be concluded that sodium hydroxide concentrations determine the magnitudes of the desirable reaction (reaction 2) and the side undesirable reactions (reactions 3 and 4) as well (**Scheme 2**).

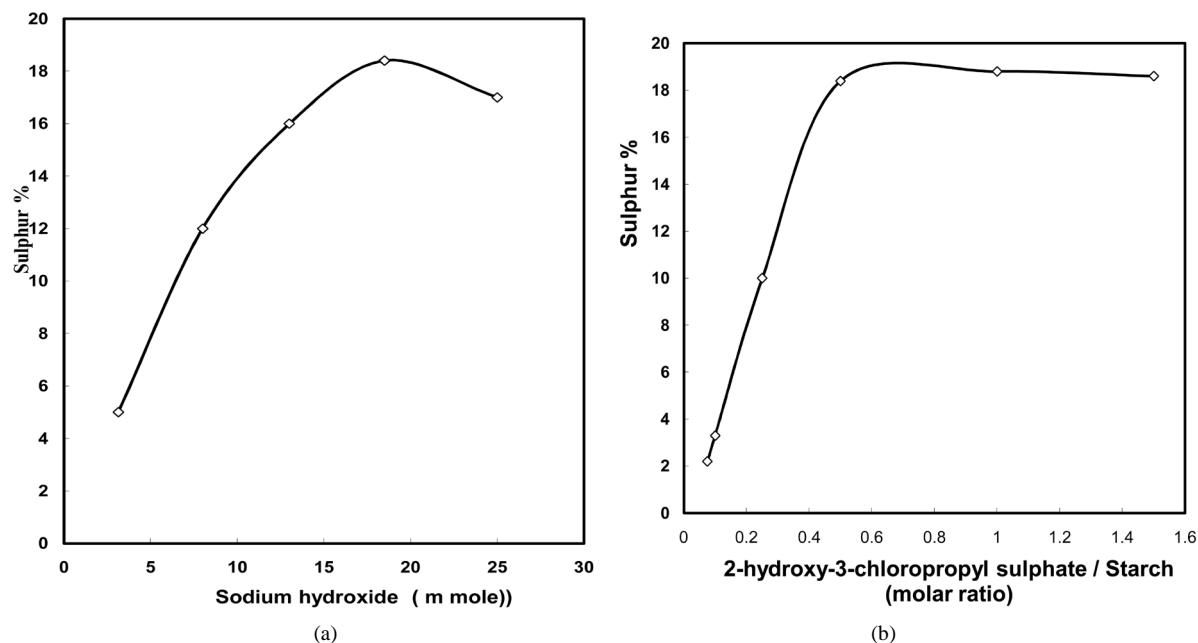### 3.1.2. Concentration of 2-Hydroxy-3-Chloropropyl Sulphate
Figure 1(b) shows the sulphur % of the starch when it was reacted with 2-hydroxy-3-chloropropyl sulphate at different concentrations. The 2-hydroxy-3-chloropropyl sulphate: starch molar ratios used were (0.125 - 1.0) with starch (25 m mole) in presence of NaOH: 2-hydroxy-3-chloropropyl sulphate molar ratio (1.5: 1) at 80˚C for 240 minutes.

Figure 1(b) discloses that the extent of the reaction increases sharply as the 2-hydroxy-3-chloropropyl sulphate: starch molar ratio increases upto 0.5 molar ratio. Further increase in concentration, specifically beyond 1.0 is accompanied by a slight increase in sulphur percent. This trend could be interpreted in terms of 1) structural changes in starch which diminish susceptibility of the latter towards further reactions; 2) shortage of accessible starch hydroxyls through their involvement in the reaction with 2-hydroxy-3-chloropropyl sulphate and 3) the possibility that 2-hydroxy-3-chloropropyl sulphate at higher concentrations are more susceptible to alkaline hydrolysis. It follows from this that using 2-hydroxy-3-chloropropyl sulphate at increasing concentration upto 0.5 molar ratio creates conditions where all these possibilities are far from achieving their negative effect after attaining the observed balance.
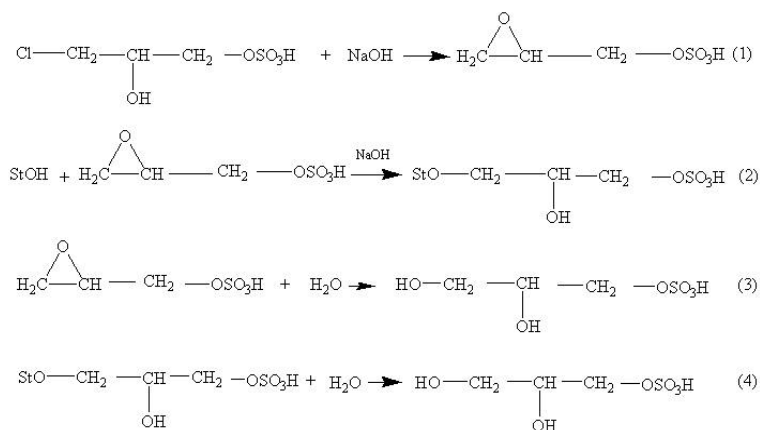
3.1.3. Durations and Temperature of the Reaction
Table 1 demonstrates the effect of duration and temperature on the extent of the reaction (expressed as sulphur %) occurring between 2-hydroxy-3-chloropropyl sulphate and starch in presence of sodium hydroxide. The starch (25 m mole) was reacted with 2-hydroxy-3-chloropropyl sulphate (12.5 m mole) for varying lengths of durations (30 - 300 min.) at different temperatures (60˚C - 90˚C). The reaction was effected under the influence of NaOH (18.75 m mole).

Results of **Table 1** shed insight on the effect of duration and temperature of the reaction of starch with 2-hydroxy-3-chloropropyl sulphate. Obviously the magnitude of the extent of the reaction is determined by the duration and temperature of the reaction. For a given temperature, the extent of the reaction increases by prolonging duration of the reaction upto 180 min. Thereafter, the extent of the reaction tends to level off provided that the temperature does not exceed 70˚C. With higher temperatures (80˚C, 90˚C) the extent of reaction de-

Figure 1. (a) Effect of sodium hydroxide concentration on the extent of reaction of starch with 2-hydroxy-3-chloropropyl sulphate, expressed as sulphur %. Maize starch (25 m mole), 2-hydroxy-3-chloropropylsulphate (12.5 m mole) at 180 min for 80˚C. (b) Effect of 2-hydroxy-3-chloropropylsulphate concentration on the extent of the reaction of starch with 2-hydroxy-3-chloropropylsulphate, expressed as sulphur %. Maize starch (25 m mole), sodium hydroxide (18.75 m mole) at 80˚C for 240 min.

Scheme 2. Sodium hydroxide concentration.

Table 1. Effect of duration and temperature on the sulphur percent.

Duration (min) Temp. ˚C	Sulphur %			
	60˚C	70˚C	80˚C	90˚C
30	15	16.6	17.2	17.6
60	16.8	17.5	18.1	18.4
90	17.2	17.6	18.2	18.1
120	17.6	17.8	18.1	17.9
180	18.0	17.5	17.9	15.4
240	18.2	17.4	17.6	-
300	18.0	-	-	-

Starch, 25 m mole; 2-hydroxy-3-chloropropyl sulphate, 12.5 m mole; sodium hydroxide, 18.75 m mole.

creases by prolonging duration beyond 180 minutes. At any event, however, the highest sulphur percent is observed with modified starch sample prepared at 90˚C for 60 min. Sulphur percent values that are very comparable to this highest value could be achieved at 80˚C for 90 min. and at 60˚C for 240 min. This state of affairs reflects the combined effect of both time and temperature on allowing more reactions between starch and 2-hydroxy-3-chloropropyl sulphate. In concomitant with this is the splitting off of the bond linking starch with the 2-hydroxy-3-chloropropyl sulphate moiety and starch as well as deactivation of the etherifying agents in question through hydrolysis under the action of alkali and heat.
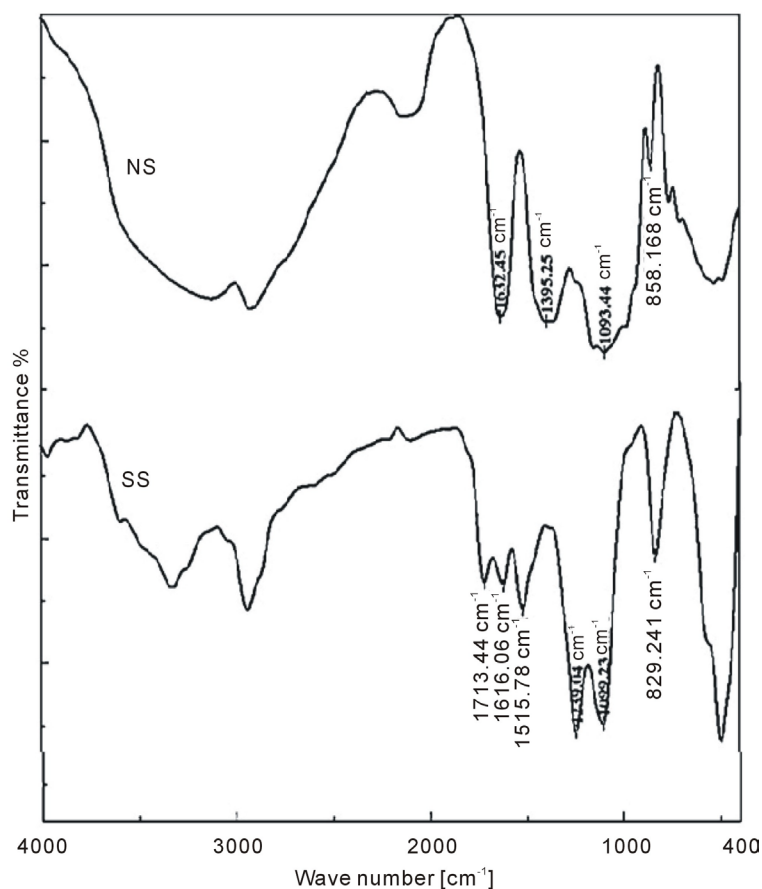
3.2. Characterization of the Starch-2-Hydroxypropyl Sulphate

3.2.1. Infra Red Spectroscopy

Native starch (NS) and starch hydroxypropyl sulphate (SS) samples having sulphur percent 18.4, were characterized by infrared (IR) spectroscopy analysis. From the IR data shown in the **Figure 2**, it can be seen that the band at 829 cm^{-1} with a shoulder at 940 cm^{-1} for a symmetrical C-O-S. These peaks cannot be found in the spectrum of the native starch sample. This can obviously powers the vibration assigned to a C-O-SO$_3$ groups on starch. The shoulder peak at 940 cm^{-1} indicated the presence of axial sulphate ester [26]-[28].
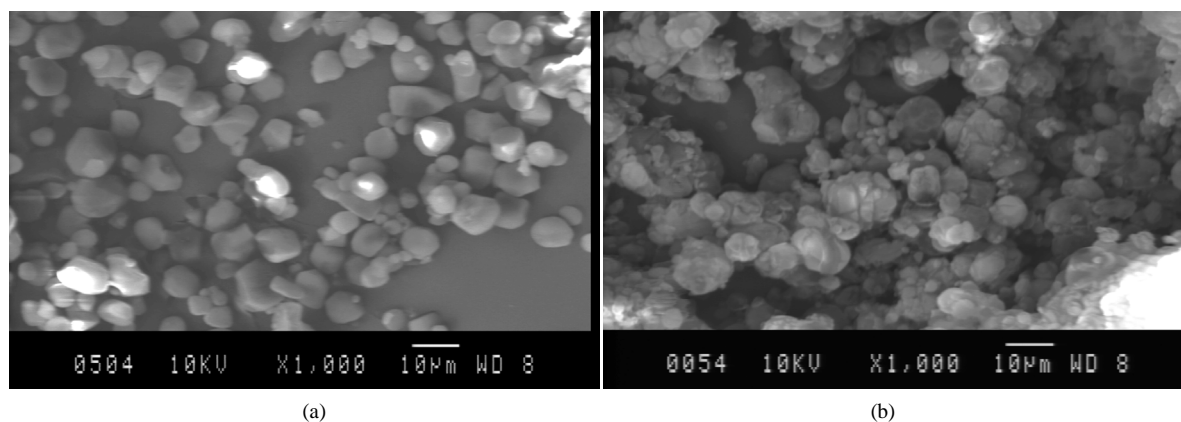
3.2.2. Scanning Electron Microscopy

Scanning electron microscopy is the right techniques used for direct observation of microstructure of spherulites of size in the range between 0.1 - 10 μm like native maize starch sample shown in **Figure 3(a)**. It is evident that the sample clearly exhibits its granular structure. Modification of starch via reaction with 2-hydroxy-3-chloropropyl sulphate, changes in contour of the granules of starch as presented in **Figure 3(b)**. It can be seen that individual granules of starch have joined through the modification process.

Figure 2. FTIR of native starch (NS) and starch hydroxypropyl sulphate (SS).

(a)   (b)

Figure 3. Scanning electron microscopy. (a) Native starch; (b) Starch hydroxypropyl sulphate.

3.3. Utilization of the Starch Hydroxypropyl Sulphate in Cationic Dye Removal

3.3.1. Initial pH

Figure 4 depicts the effect of initial pH on dye sorption value using starch hydroxypropyl sulphate. Dye adsorption was carried out using starch (0.4 g/50ml) having sulphur content of 18.4% during 70 min. duration. Dye concentration (100 ppm) was examined over of pH value ranging from 2 to 10. Results of **Figure 4** signify that the percent value of dye removal increases sharply as the pH increases from 2 to 7 then decreases also sharply thereafter. This is rather logical since at low pH, higher adsorption is associated with increased protonation by the neutralization of the negative charges at the surface of the adsorbent, which, in turn, facilitates the diffusion process and provides more active sites for the adsorbent [7]. At high pH, the dye becomes protonated and the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites is established and results in decreased adsorption.
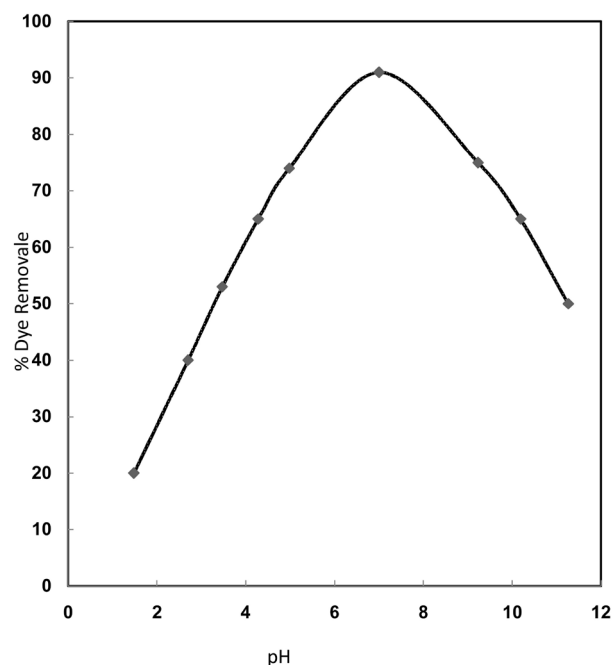
3.3.2. Contact Time of Duration and Initial Dye Concentration

The uptake of MB onto starch hydroxypropyl sulphate as a function of dye concentration was studied using starch (0.4 g/50ml) acquiring sulpher % of 18.4 and pH 7. The results obtained are summarized in **Table 2**. By and large the effect of increasing the dye concentration is to decrease the % dye removal. On the contrary prolonging the duration of contact between the dye and the starch derivative in question increases the % dye removal. For instance, 100% dye removal could be attained with an initial dye concentration of 75 ppm after 70 min. On the other hand, 100% dye removal could be achieved after 90 min. and 120 min. with initial dye concentrations of 100 ppm and 125 ppm respectively. This full (100%) removal of the dye could be observed with initial dye concentrations higher than 125 ppm even after 120 min. contact time.

The general tendency of the % dye removal to decrease particularly when the contact time between MB and starch hydroxypropyl sulphate is longer than 40 min., is a manifestation of the increase in the deriving force of the concentration gradient with the increase in the initial dye concentration [29]. The results (**Table 2**) reveal also that the uptake of MB onto starch hydroxypropyl sulphate increases by increasing the contact time (10 - 120 min.). It is understandable that initial adsorption is rapid because the adsorption of the dye occurs initially onto the exterior surface, after that dye molecules enter into pores (interior surface), a relatively slow process [30]. 100% dye removal could be arrived at when initial dye concentrations of 75, 100 and 125 ppm were allowed to be in contact with starch hydroxypropyl sulphate for 70, 90 and 120 min. respectively.

3.3.3. Adsorbent Dose

Table 3 shows the % dye removal as function of adsorbent concentration. The adsorption of the dye on starch hydroxypropyl sulphate at different concentrations of the latter (0.1 - 0.5 g in 50 mL) was investigated. Starch hydroxypropyl sulphate at 70 min. was used. Dye concentration (75 ppm) with sulpur percent 18.4 and at pH 7 were employed for performing dye adsorption. Results of **Table 3** show that % of dye removal increases as the adsorbent concentration increases due to the availability of larger surface area with more active functional groups at higher adsorbent dosages.

Figure 4. Effect of pH on the dye removal %. Starch hydroxypropyl sulphate (0.4 g/50ml) acquiring sulphur % of 18.4 after 70 min, dye concentration (100 ppm).

Table 2. Effect of contact time of duration and initial dye concentration on % of dye removal.

concentration Duration (min)	% of dye removal at 75 (ppm)	% of dye removal at 100 (ppm)	% of dye removal at 125 (ppm)	% of dye removal at 150 (ppm)	% of dye removal at 175 (ppm)	% of dye removal at 200 (ppm)
10	45	48	52	55	60	63
20	56	58	60	60	61	60
30	66	66	66	64	63	62
40	77	79	73	68	68	68
50	86	83	79	72	70	69
60	94	87	84	75	72	70
70	100	91	89	78	74	71
80	-	95	93	80	75	72
90	-	100	96	82	76	73
100	-	-	98	84	77	74
110	-	-	99	86	78	75
120	-	-	100	87	79	75

Starch hydroxypropyl sulphate at pH 7 and sulphur % 18.4.

Table 3. Effect of adsorbent dose on % of dye removal.

adsorbent concentration (g in 50 ml)	% of dye removal
0.1	60
0.2	70
0.3	80
0.4	90
0.5	100

Starch hydroxypropyl sulphate at 70 min, dye concentration (75 ppm) with sulphur percent 18.4 and at pH 7.

Table 4. The effect of sulphur percent of on % of dye removal.

Sulphur percent	% of dye removal
6.5	45
10.4	60
14.1	75
16.2	89
18.4	100

Starch hydroxypropyl sulphate at pH 7, 70 min, dye concentration (75 ppm).

3.3.4. Sulphur Percent

Table 4 displays the % dye removal using starch hydroxypropyl sulphate acquiring different sulphur percents at 70 min, dye concentration (75 ppm) and at pH 7.

Results of Table 4 feature that the dye removal % increases by increasing the sulphur percent of the adsorbent. This is unequivocally due to the presence of more active functional groups *i.e.* hydroxypropyl sulphate, in the molecular structure of starch. Needless to say that the sulphur percent is a measure of these functional groups; the higher the sulphur percent is, the higher the functionality of the starch derivatives in question is.

4. Conclusions

Starch hydroxypropyl sulphate was synthesized using the dry process under a variety of conditions. Factors studied included catalyst concentration and 2-hydroxy-3-chloropropyl sulphate concentration as well as duration and temperature. Based on the results obtained, the best conditions for synthesis of starch hydroxypropyl sulphate derivatives were established; they were 2-hydroxy-3-chloropropyl sulphate: starch molar ratio 0.5:1, sodium hydroxide: 2-hydroxy-3-chloropropyl sulphate molar ratio 1.5:1, at 90°C for 60 min. Under such conditions, starch hydroxypropyl sulphate with sulphur percent 18.4 could be achieved. Characterization of thus modified starch via IR spectroscopy analysis and scanning electronic microscope was investigated and, difference in contour of the starch granules was verified.

The as-prepared starch hydroxypropyl sulphate derivatives acted as cationic dye removal. The goal was realized starch hydroxypropyl sulphate which had sulphur percent of 18.4 at pH 7. 100% dye removal could be achieved at dye concentrations of 75, 100 and 125 ppm after a contact time of 70, 90 and 120 min respectively in presence of the newly synthesized adsorbent at a concentration of 0.5g in 50 mL.

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