

Upgrading the Commercial Phosphoric Acid using the Cross Linked Starch

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Summary: The green phosphoric acid produced from Abu Zaabal for Fertilizers and Chemicals Company (Egypt) contains 44% P_2O_5 . The acid is heavily entrained with impurity cations, among which arsenic, cadmium and uranium are the most toxic. In addition, anion like chloride, fluoride and sulfate must be considered. The present work is a trial to get the benefit of the decolorization character of starch as a poly-heterocyclic compound to remove the green color, florid and some impurities elements from the commercial phosphoric acid to be suitable for food industry. The water insoluble polyamine has predominantly tertiary amine groups which may be produced. The chemical reaction of epichlorohydrine [E] with different amines $R-NH_2$, $R-NHR$ (primary or secondary amines) has been applied cross bonded with starch. The formed amphoteric exchanger resin starch is proved by the I.R. chart and a likely clear phosphoric acid is obtained.

Introduction

Phosphoric acid is an important intermediate between phosphate ores and major end products such as ammonium phosphate, triple super phosphate, liquid fertilizers and some types of nitric phosphates. In the chemical field, phosphoric acid is an intermediate in the production of materials such as detergents, surface treatment chemicals, beverages, dentistry tooth pastes, fire extinguishers and water treatment. The wet process turns out phosphoric acid with P_2O_5 , fluorine and small amounts of sulfur compounds, e.g. calcium, aluminum and silicon besides iron, lanthanides, uranium and some other compounds. One of disadvantages of phosphoric acid produced by the wet process is its high content of mineral impurities in specific applications.

Phosphoric acid has many applications in different industrial, agriculture, food and pharmaceutical industry. The purity of grade determines

the use of extractants, such as ketones, tributyl phosphate (TBP), triocylphosphine oxide (TOPO), N-oxides, sulfoxides, etc. In the other phosphoric acid for certain purpose as well as its price. For example, green acid is used in fertilizer and high purity acid in food and pharmaceutical industries. This is the most important grade of phosphoric acid which has a wide use in phosphate salts making, metal surface treatment (car industry), food uses in animal feeding, cooking oil, detergent, in soft drinks (Coca Cola etc.), tobacco, chemicals reagents industry, analytical reagents, sugar decolorizing, pharmaceutical and electronic industry.

The aim of this work is to upgrade the commercial phosphoric acid to a slightly pure one suitable for food industry using a material simply treated, available in the local market, cheap and effective. The industrial use of the chemically modified starches is numerous. One of these potential application series is in the biodegradable anion or cation (amphoteric exchanger) which is suitable for decolorization of textile waste waters⁽¹⁾.

Experimental

Procedures:

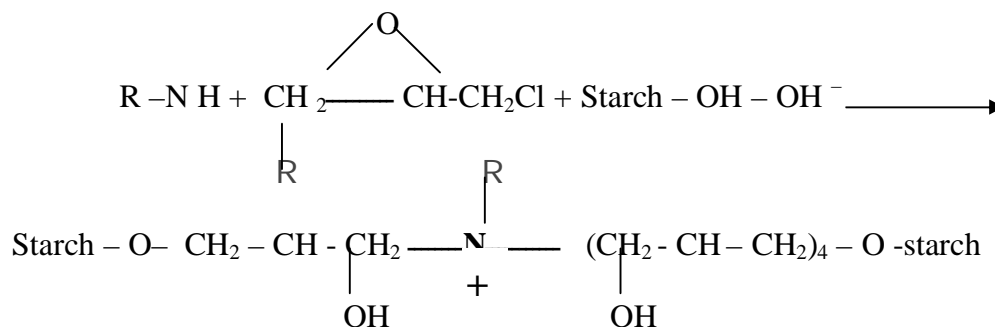
The preparation of cross linked starch took place in glass vials (250 ml) under vigorous stirring at room temp, for 18 hours in units of molar ratio and chemical listed in Table (1). The obtained polymer residue was grinded to -60 mesh size and washed with water till neutralization occurred; examined with pH paper^(2,3). Then the residue was washed by 96% ethanol, giving a new ion exchanger.

A glass column of 25 cm long and internal diameter 1.0 cm wide was packed by 5g. (-60 mesh size) of the treated starch making about 10 cm height. From these parameters, the obtained wet settled resin equals to 7.85 cm. The column was feeded with commercial phosphoric acid provided from Abu

Zaabal for Fertilizers and Chemicals Company (Egypt); at a flow rate very slow about 2 was properly crystallized from hexane. Next, it was reacted under reflux with aminotriazole in ethanol for 6 hours followed by the addition of ml per hour. The used phosphoric acid (50 ml) was allowed to pass through the resin for five cycles to give the likely clear acid. All the chemicals used were of commercial grade.

Results and discussion

Cross linking of starch with epichlorohydrine [E] is the most common method used in the polysaccharide chemistry⁽⁴⁾. The chemical reaction of epichlorohydrine [E] with different amines R-NH₂, R-NHR (primary or secondary amines) has been applied cross bonded with starch⁽²⁾. In this way, the produced water insoluble polyamine has predominantly tertiary amine group which may be produced according to the following suggested reaction:



The resulted material may be biodegradable having counter ions that are very cheap than synthetic petroleum based. The formed anion exchanger resin starch is proved by measuring the I.R. spectra.

The physical properties of the modified starch are tabulated in Table (1) including minimum molar ratios. S.A: secondary amine: NaOH: water are 0.01: 0.01: 0.005: 0.005: 0.2 respectively. 90% yield compared with starch. NaOH plays a role in the activation of hydroxyl group and transporting chemicals (2&5).

Sample No. 5 is the best one which has the optimum yield percentage; it is also more solid product that can be easily grinded to the required mesh size. This product is suitable to react as resin, due to its surface area facilitated the adsorption of fluorine and some other elements found in the commercial phosphoric acid Table (2). Comparison between the obtained phosphoric acid of Abdel Khalek et al., 2008 ⁽⁶⁾, which produced by treating the same commercial phosphoric acid is shown in Table (3). The difference in shape and appearance between the native starch and the cross linked one can be noticed in Fig. (1). I.R. analysis of starch both the industrial and the treated one are shown in Fig. (2), eventually, a likely clear phosphoric acid is obtained (Fig.3).

Table (1): Results of cross linked corn starch with different amines in mol unit.

Sample NO.	E	Starch	Amine type-mole	NaOH	H ₂ O	Yield (native starch) (times)
1	0.01	0.01	Diethyl amine (0.005)	0.005	0.2	0.90 ^e
2	0.01	0.01	n-octyl amine (0.005)	0.005	0.2	1.11 ^e
3	0.02	0.01	n-octyl amine (0.005)	0.005	0.2	2.00 ^e
4	0.025	0.01	n-octyl amine (0.005)	0.005	0.2	2.11 ^e
5	0.025	0.01	n-octyl amine (0.01)	0.005	0.2	2.27 ^e

e = water insoluble residue.

I.R. spectra of cross linked starch and elemental analysis:

Native and cross linked starch samples were prepared using the KBr pellet method. IR spectra were recorded at wave number ranges between 400 and 4000 cm⁻¹.

In the spectra of native starch (Fig. 2), there are several noticeable absorption bands at 1159, 1082, 1014 cm^{-1} , which were attributed to C–O bond stretching ^(7 & 8). Also there are absorption bands at 992, 929, 861, 765, 575 cm^{-1} due to the entire hydroglucose ring stretching vibrations. A very broad band due to hydrogen bonded hydroxyl groups appeared at 3421 cm^{-1} ⁽⁹⁾.

The treated cross linked starch (Fig. 2), recorded new absorption bands at 2924 cm^{-1} for C-H aliphatic, also at 1647, 1557 cm^{-1} for C-N and the hydroxyl group band appeared sharp at 3420.6 cm^{-1} due to the increase of the cross linked bond.

Table (2): Chemical analysis of the obtained phosphoric acid along 5 cycles.

Cycle Coptd.	1	2	3	4	5	H ₃ PO ₄	Crude H ₃ PO ₄
Wt. %							
P ₂ O ₅	49	52	57	57.8	57.8	57.8	44
Fe ₂ O ₃	2.0	1.9	1.7	1.5	1.3	1.3	2.5
Al ₂ O ₃	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	0.66
SiO ₂	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	0.98
F	0.41	0.23	0.19	0.12	0.06	0.05	0.87
MgO	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	1
CaO	u.d.	u.d.	u.d.	u.d.	u.d.	u.d.	0.3
ug/ml							
Mn	318	154.7	72.8	45.5	25.48	111	728
U	36.4	10.92	4.55	u.d.	u.d.	6.37	60.1
Cd	7.28	3.82	1.73	1.37	0.146	0.22	13.65
Cu	22.75	9.1	1.37	0.46	0.22	2.51	36.4
Zn	91	45.5	10.92	6.37	5.0	23.26	

u.d. = under detection limit

Table (3): Comparison between chemical analyses of the obtained likely

clear acid and the published one of Abdel Khalek et al., 2008 ⁽⁶⁾.

Component	Obtained clear phosphoric acid	Published acid
P ₂ O ₅ %	57.8 %	62.0 %
Fe ₂ O ₃	1.3 %	7.7%
Al ₂ O ₃	u.d.	-
SiO ₂	u.d.	-
F	0.05 %	0.002 %
MgO	u.d.	-
U	6.37 ug/ml	-
CaO	u.d.	-
Cd	0.22	u.d.
Cu	2.51	u.d.
Zn	23.26 ug/ml	0.91 ug/ml
Mn	111 ug/ml	0.091 ug/ml

u.d. = under detection limit

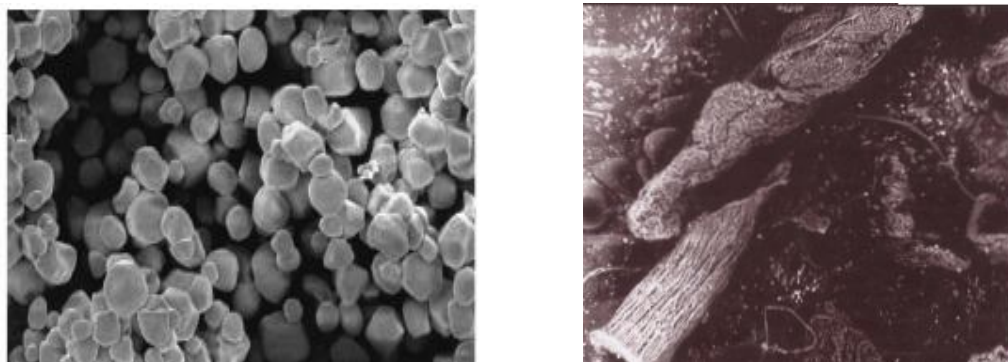


Fig. (1): Photograph showing the difference between the native starch (left) and cross linked treated starch (right).

Cross linked starch

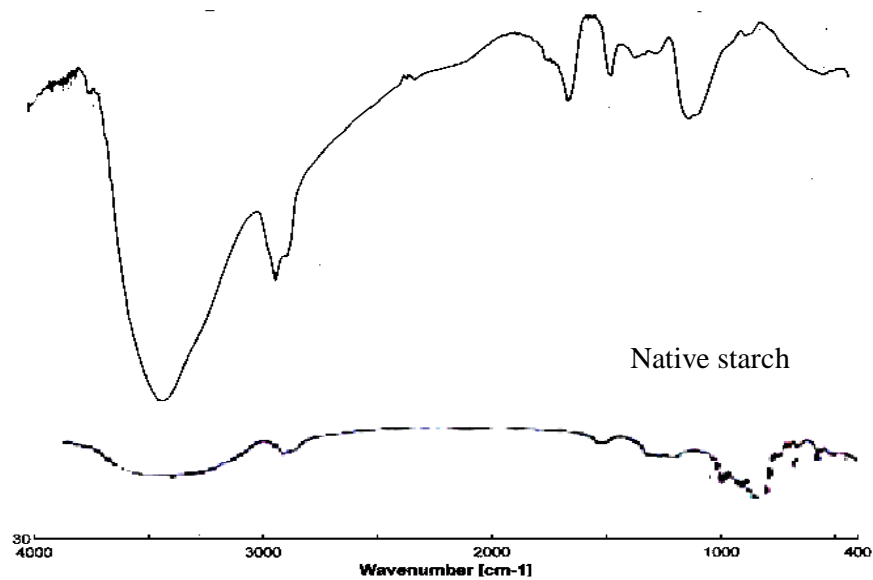


Fig. (2): I.R. spectra for the native used starch and the cross linked starch.



Fig. (3): Photograph showing the difference between the commercial phosphoric acid (to the left) and the obtained clear one.

References

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