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ORIGINAL ARTICLE

Application of Oxidized Cornstarch as a Nonphosphoric Detergent Builder

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Abstract Oxidized cornstarch, which is only composed of carbon, hydrogen and oxygen elements, was used as a builder in detergent formulations to reduce the hardness of water. Therefore, the calcium binding capacity of these oxidized cornstarch samples was tested and the relative detersive efficiency of the self-made detergent with oxidized cornstarch builder was also evaluated. The results show that higher Ca^{2+} binding capacities 104.5 mg/g can be obtained when the synthesis is carried out at 100 °C for 3 h in conjunction with the addition of 21 g NaOH. The detersive efficiency can reach 1.28 which is equivalent to the other detergent powders. In addition, the biodegradability of the oxidized cornstarch was judged as being adequate by the China National Center for Quality Supervision and Test of Plastic Products. Compared with the traditional detergent builders, the oxidized cornstarch is water-soluble, environmentally friendly, and cheap, with an equivalent performance to traditional detergent builders.

Keywords Detergent · Builder · Oxidized cornstarch · Biodegradability

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Introduction

Surfactant efficiency is greatly reduced in hard water and surfactants do not show good performance even in softer water. Furthermore, large amounts of surfactants in detergents not only significantly increase biological demand in water but also impose a heavy load on sewage works and on the environment due to their eco-toxicity. To remove Ca^{2+} and Mg^{2+} ions existing in hard water, and thus to lower the content of surfactant in the detergent formulations, detergent builders are often used. A potential builder should satisfy a large number of requirements, including sequestering ability, alkalinity, buffer capacity, and other environmental and economic practicability [1].

Traditionally, the detergent builder has commonly been a phosphate, such as sodium tripolyphosphate (STPP). However, phosphates are excellent fertilizers for algae, bacteria, and other flora and fauna in rivers, lakes and oceans, making them bloom at very rapid rates, exhausting the oxygen supply both at the surface and in the bottom layers of water bodies, and killing fish. This phenomenon so-called eutrophication [2–4], has led to international agreements aimed at banning or limiting phosphate use in detergents [5–8].

Subsequently, other water softeners such as sodium carbonate, sodium silicate, nitrilotriacetic acid (NTA), ethylene diamine tetraacetic acid (EDTA) and zeolites were used as a substitute for STPP. Although sodium carbonate- and sodium silicate-built detergents show almost the same performance as the leading phosphate formulations, their high alkalinity is harmful to our skin and eyes. In addition, they produce deposits on fabrics, which trap dirt and provide a breeding ground for bacteria, and cause washed fabrics to become harsh, grey, and to wear out more quickly [9]. NTA has been proved to be quite toxic when contaminated with heavy metals in drinking water, and EDTA has poor biodegradability characteristics [10, 11]. Zeolites have other negative features. For example, zeolites are water-insoluble and less alkaline than STPP and therefore require the use of other builders such as the costly sodium citrate to compensate [12].

Our group has reported research work on the oxidation of corn starch using oxygen as oxidant without a catalyst [13]. This work presents experimental results on the partial substitution of STPP by water-soluble oxidized cornstarch (WOC) in a heavy-duty household washing detergent powder. The objective of the present study was to determine whether appreciable quantities of WOC can be used without appreciably altering the overall characteristics of the detergent product. The price of STPP on the world market is about two to three times that of the oxidized cornstarch, so the cost-effectiveness of the oxidized cornstarch is an issue to consider. Furthermore, its advantages over other builders lie in its favorable water-solubility, high calcium binding capacity, good detergency performance and eminent biodegradability.

Materials and Methods

Materials

Cornstarch was supplied by Dacheng Corn Industrial Group Co., Ltd, Changchun, China. Sodium hydroxide (Guaranteed reagent), hydroxylamine chloride, AES (lauryl ether sulfate), Na_2SiO_3, Na_2CO_3 and Na_2SO_4 were all analytical reagents and purchased from Beijing Chemical Plant, China. Oxygen was commercial pure.

Experimental

Preparation of Water-Soluble Oxidized Cornstarch (WOC)

WOC was prepared by the oxidation of cornstarch as reported elsewhere [13].

Determination for Calcium Binding Capacity of WOC

The calcium binding capacity of the oxidized cornstarch prepared under different conditions was determined by a calcium ion selective electrode and a calomel normal electrode with the standard addition method. Samples were run in triplicate and the variation coefficient was 1%.

Detergency Experiment of Oxidized Cornstarch as Detergent Builder

The detersive power of oxidized starch as a detergent builder was evaluated by method GB13174-91 (National Standard of China). The whiteness value was determined with a WSC-S colorimeter (made by the Shanghai Precision and Scientific Instrument Company Limited, People's Republic of China). The formula used to calculate the detersive power is: $R = (F_2 - F_1)/(F_0 - F_1) \times 100\%$

F_0 Spectral reflectance of uncontaminated white cloth, %;
F_1 Spectral reflectance of contaminated cloth before washing, %;
F_2 Spectral reflectance of contaminated cloth after washing, %;
R_0 Detersive power value of normal detergent, %;
R Detersive power value of testing sample detergent, %

The relative detersive ratio value of the detergent is $P = R/R_0$.

Biodegradability Experiment of WOC

Biodegradability of WOC was assessed by the China National Center for Quality Supervision and Testing of Plastic Products according to the Chinese National Standard (GB/T 19277-2003), which is the same as ISO 14855:1999. The determination was under controlled composting conditions—the method was by analysis of evolved carbon dioxide. The amount of the cumulative carbon dioxide evolved is determined by measuring the dissolved inorganic carbon (DIC) after complete absorption in a sodium hydroxide solution. In a typical case, composting vessels which have a volume of about 3 L are prepared; then an amount of inoculum is added (as shown in Table 1) containing 600 g of total dry solids and an amount of WOC containing 100 g of dry solids and this is then mixed well. One hundred and twenty milliliters of distilled water is added to the mixture to make it somewhat sticky and to have enough free water so that it can be expressed when gently pressed by hand. Then the mixture is poured into the composting vessels. Then the composting vessels are placed in the test environment at (58 ± 2) °C. The system is continuously aerated with previously saturated water and carbon-dioxide-free air. The reference material (cellulose) is handled in the same way as the test material. The vessels for the blank contain only inoculum, and should have the same amount of total dry solids as the vessels with the test material.

Table 1 The basic character of the inoculum

Inoculum (g)	Total dry solids content (g)	Water content (g)	Volatile-solids content (g)	C/N
600.00	437.62	162.38	126.32	14.8

Calculation of the Theoretical Amount of Carbon Dioxide

The theoretical amount of carbon dioxide $ThCO_2$, is calculated in grams per vessel which can be produced by the test material using Eq. 1:

$$ThCO_2 = M_{TOT} \times C_{TOT} \times 44/12 \quad (1)$$

where, M_{TOT} is the total dry solids in grams, in the test material introduced into the composting vessels at the start of the test; C_{TOT} is the proportion of total organic carbon in the total dry solids in the test material, in grams per gram; 44 and 12 are the molecular mass of carbon dioxide and the atomic mass of carbon, respectively.

Calculation of Percentage Biodegradation

From the cumulative amounts of carbon dioxide released, the percentage biodegradation D_t of the test material is calculated for each measurement interval using Eq. 2:

$$D_t = \{(CO_2)_T - (CO_2)_B\} \times 100/ThCO_2 \quad (2)$$

where, $(CO_2)_T$ is the cumulative amount of carbon dioxide evolved in each composting vessel containing test material, in grams per vessel; $(CO_2)_B$ is the mean cumulative amount of carbon dioxide evolved in the blank vessels, in grams per vessel; $ThCO_2$ is the theoretical amount of carbon dioxide which can be produced by the test material, in grams per vessel.

Results and Discussion

Calcium Binding Capacity of WOC

Oxidized starch is one kind of amylose containing carboxyl with the ability of complexing metallic ions [14]. It can treat hard water by complexing Ca^{2+}, Mg^{2+} etc. in water, as an auxiliary to the detergent in the washing-powder.

The calcium binding capacity of WOC is changed with the synthesis conditions (amount of NaOH, reaction temperature and reaction time) and the mass fraction of the oxidized cornstarch solutions. As shown in Fig. 1, for the same mass fraction of the oxidized cornstarch solutions, the calcium binding capacity increases with an increasing amount of sodium hydroxide up to 21 g, and then decreases with further increases in the amount of sodium hydroxide. The influence of the reaction temperature on the calcium binding capacity of the product is presented in Fig. 2. For the same mass fraction of the oxidized cornstarch solutions, the calcium binding capacity of the oxidized cornstarch is the highest when it is prepared at 100 °C. From Fig. 3, it can be seen that the optimal reaction time is 3 h; at that

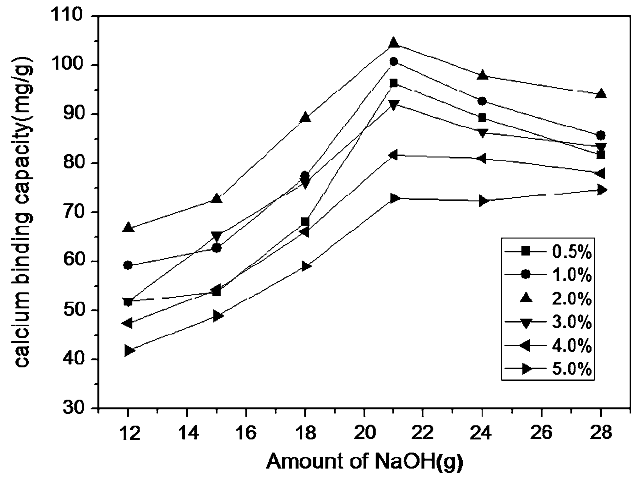

Fig. 1 Effect of the amount of NaOH (g) on the calcium binding capacity of different mass fraction (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0%) oxidized cornstarch solution

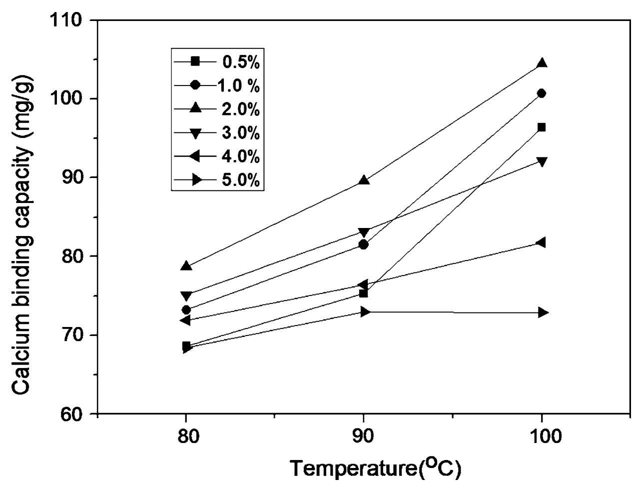

Fig. 2 Effect of reaction temperature (°C) on the calcium binding capacity of different mass fraction (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0%) oxidized cornstarch solution

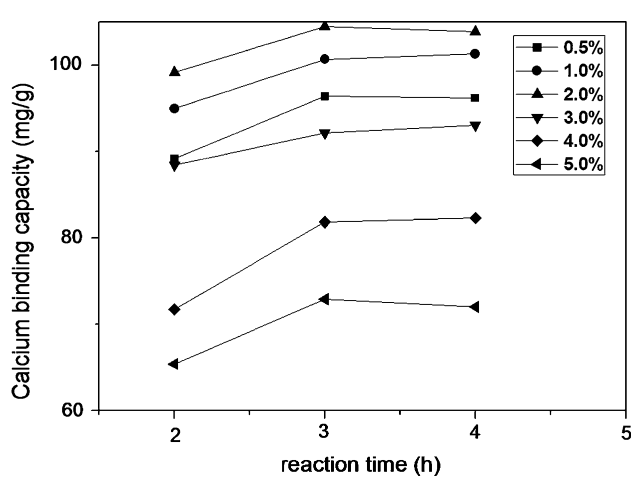

Fig. 3 Effect of reaction time (h) on the calcium binding capacity of different mass fraction (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0%) of oxidized cornstarch solution

Table 2 Calcium binding capacity of different detergent builder

Builder	Oxidized cornstarch	EDTA[a]	Sodium tripolyphosphate[a]	Poly(acrylic acid)[b]
Calcium binding capacity (mg/g)	104.5	109	107	98.5

[a] Data from Ref. [16]

[b] Data from Ref. [17]

Table 3 Relative detersive ratio values (*P*) of the self-made detergent with different content water-soluble oxidized cornstarch (WOC)

The content of WOC (%)	10	15	20	25	30	35	40
P	1.20	1.22	1.23	1.25	1.28	1.26	1.26

Table 4 The detersive effect contrast between self-made detergent and other detergents available on the Chinese market

Detergents	Self-made	White cat	Keon	OMO	Ariel	Tide	Nice
pH (1% solutions)	10.33	10.29	10.41	10.30	10.32	10.32	10.40
P	1.28	1.25	1.33	1.26	1.28	1.27	1.30

time, the calcium binding capacity is the highest for the same mass fraction of the oxidized cornstarch solutions. In conclusion, 21 g NaOH, at 100 °C and for 3.0 h are the optimum conditions for attaining the desirable oxidized starch with the highest calcium binding capacity—104.5 mg/g, and these conditions are in agreement with the optimum preparation conditions for the highest carboxyl content of oxidized starch reported earlier [13]. It is obvious that the higher the carboxyl content of obtained oxidized starch is, the stronger is its calcium binding capacity. In addition, the calcium binding capacity of WOC is equivalent to other detergent builders (Table 2), which implies that it is suitable for use as an alternative to phosphoric builders.

Note that the calcium binding capacity increases when the mass fraction of the oxidized cornstarch solutions is increased from 0.5 to 2%, while it decreases when the mass fraction of the oxidized cornstarch solutions is beyond 2% (Figs. 1, 2, 3). Therefore, the optimum mass fraction of the oxidized cornstarch solutions is 2%. This is probably due to the fact that the chains of the oxidized cornstarch cannot be fully stretched open in higher concentration solutions, which makes the calcium binding ability decline.

Relative Detersive Efficiency of the Self-Made Detergent with Oxidized Cornstarch Builder

According to the usual formulations of detergent powders, the builder content should be 10–40% of the whole [15]. Therefore, the powder detergent was formulated with AES (lauryl ether sulfate) as surfactant, Na_2SiO_3, Na_2CO_3, Na_2SO_4, and self-synthesized oxidized cornstarch. The relative detersive ratio values of detergent (P) with different contents of WOC are shown in Table 3. From Table 3, it can be seen that P increases with the content of builder WOC, and the detersive effect is the best for a 30% WOC content. P can reach 1.28 when the composition of the detergent formulation (in wt%) was as follows: AES (9.0), Na_2SiO_3 (4.5), Na_2CO_3 (5.5), Na_2SO_4 (51.0), WOC (30.0).

In order to measure the detersive efficiency of the tested detergent, it was checked against other detergent powders available on the Chinese market (Table 4). From Table 4, it can be concluded that the pH (namely buffering capacity) and relative detersive ratio value (detersive efficiency) of the tested detergent powders are equivalent to those of the market products. Therefore, WOC can be used as a builder without appreciably altering the overall characteristics of the detergent product. WOC has been also used to substitute STPP for preparing 10 tons of detergent powders by Shijiazhuang Weina Bang Daily Chemical Co., Ltd. and Taiyuan Detergent Development Co., Ltd. of China, and then the nonphosphoric detergent powders were inspected by the National Cleaning Products Quality Supervision and Inspection Center. The inspection results supplied by the National Cleaning Products Quality Supervision and Inspection Center are shown in Table 5. From Table 5 it can be concluded that 7 projects were inspected and 7 projects were judged qualified. Therefore, WOC is feasible to be used as a substitute for STPP..

Biodegradability of WOC

The carbon dioxide evolution and biodegradation curves are shown in Figs. 4 and 5 respectively. Figure 4 shows that the CO_2 production in the blank vessels after 10 days is 18.72 g, and thus the mean CO_2 production in the blank vessels after 10 days per gram volatile solids is (18.72/126.32) = 148.2 mg which is in the range 50 mg to 150 mg. Furthermore, from Fig. 4 it can be concluded that the degree of biodegradation of reference material after 45 days is 75.23%, which is larger than 70% which is the validity level. Figure 5 shows that the ultimate (91 days) degree of biodegradation of WOC is 70.4%, so it is valued qualified. Therefore, the WOC is not only nonphosphoric but is also biodegradable.

Table 5 Inspection report on the nonphosphoric detergent powder supplied by National Cleaning Products Quality Supervision and Inspection Center

Serial number	Testing project and its unit	Technical requirement (WL-A type)	Test result	Single judgment
1	Appearance	Powders or particles that haven't agglomerated	Yellow particles that haven't agglomerated	Qualified
2	The content of total actives (%)	≥13	19	Qualified
3	Apparent density (g/cm^3)	≥0.30	0.71	Qualified
4	pH (25 °C, 0.1% solution)	≤11.0	10.5	Qualified
5	The content of free base (with NaOH account)	≤10.5	3.4	Qualified
6	The content of P_2O_5	≤1.1	<0.1	Qualified
7	Dirty cloth detergency requirements[a]	JB-01 ≥Detergency of standard detergent powder	>Detergency of standard powder	Qualified
		JB-02 ≥Detergency of standard detergent powder	>Detergency of standard powder	
		JB-03 ≥Detergency of standard detergent powder	>Detergency of standard powder	

[a] Test concentration: standard detergent powders 0.2%, samples 0.2%

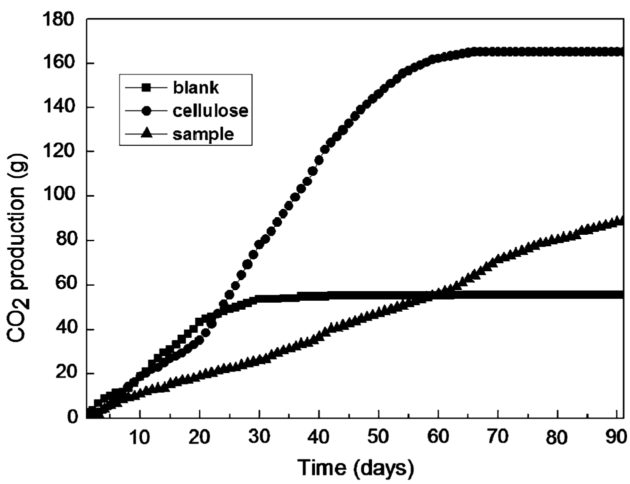

Fig. 4 Carbon dioxide evolution curves of the water-soluble oxidized cornstarch and cellulose

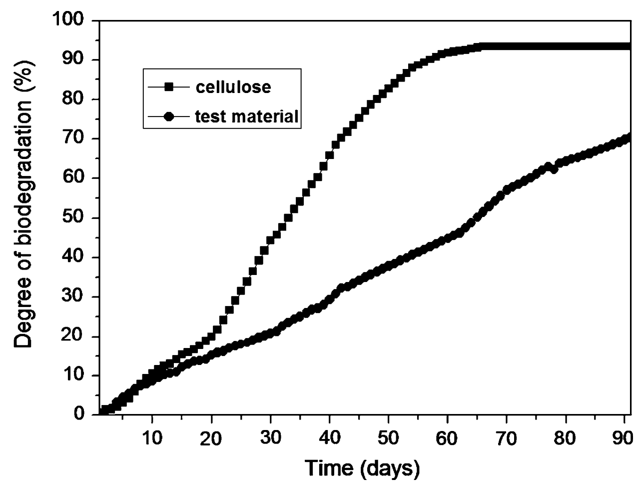

Fig. 5 Biodegradation curves of the water-soluble oxidized cornstarch and cellulose

Conclusion

This paper presents the applied research study of water-soluble oxidized cornstarch as a detergent builder. The results show that oxidized cornstarch can be used as a detergent builder without altering the overall characteristics of the detergent product. The optimum preparation conditions for the oxidized cornstarch as detergent builder are as follows: 21 g NaOH, reaction time 3 h and the reaction temperature 100 °C. Under these conditions, its calcium binding capacity attains 104.5 mg/g, essentially the same value as for other builders. Detergent powders have been compounded with the oxidized cornstarch as builder and for the best recipe of the tested detergent powder, the pH and detersive effect compete with products available on the Chinese market. Moreover, the synthesized oxidized cornstarch is nonphosphoric, biodegradable, water soluble and cheap, and is thus going to be used soon as a detergent builder.

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