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Reaction Mechanism and Kinetics Study of Wheat Polysaccharide via Modified Reductor Technique in Bead Making Process

C. A. Idibie (Corresponding Author)
Department of Chemical Sciences, Faculty of Science, Edwin Clark University, Kiagbodo
Email: krisid2007@yahoo.com

K. J. Awatefe
Department of Chemical Sciences, Faculty of Science, Edwin Clark University, Kiagbodo

P. D. Clark
Department of Chemical Sciences, Faculty of Science, Edwin Clark University, Kiagbodo

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Abstract

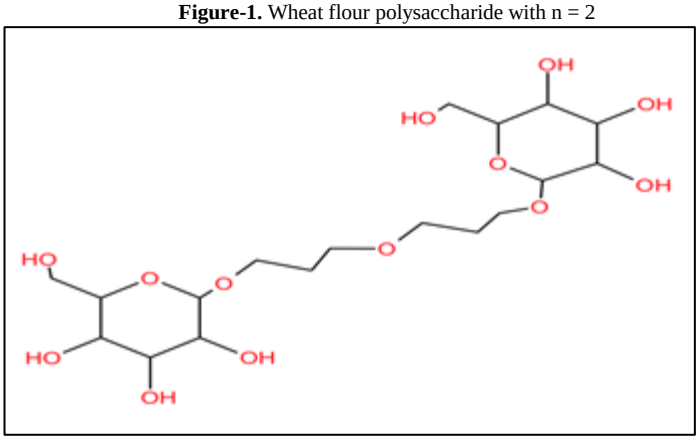
The reaction mechanism and kinetics investigation of the substitution of titanium in wheat flour polysaccharide (referred to here as titaniumation) in aqua medium during bead making process was carried out. The use of the Modified Reductor Technique was implored to study the reaction kinetics. The study was carried out at varying temperatures between 25 – 70^{o}C. The study showed that the titaniumation of the wheat polysaccharide molecules increased with time and temperature. Hence, at 25^{o}C, the degree of titaniumation (DT) of the ring increased from 0.41 % to 0.49 % and at elevated temperature of 70^{o}C, DT increased from 0.58 to 0.94 % as time progressed from 30 to 210 mins, respectively, while keeping both amount of wheat polysaccharide and TiO_2 constant, and thus achieving >1.9-fold. This also implies that the titaniumation of wheat polysaccharide using TiO_2 is favourable at elevated temperature. The study was able to reveal that the reaction mechanism of the titaniumation of the polysaccharide molecules is an electrophilic substitution reaction, favouring the ortho position, while the kinetics study showed that the titaniumation reaction is of first order reaction.

Keywords: Polysaccharide; Mechanism; Kinetics; Wheat; Flour; Titanium; Titanium dioxide; Reductor.

1. Introduction

Wheat flour is mainly composed of starch, a macromolecule in the form of polymer. Starch as a polysaccharide (complex carbohydrate) consists of a chain of glucose molecules (Figure 1), joined together in covalent bonds. It is known with a basic chemical formula of $(C_6H_{10}O_5)_n$, where n is the number of bonded glucose molecules that elongates the chain.

Figure-1. Wheat flour polysaccharide with n = 2



Polysaccharides belong to the class of biological macromolecules that is generally made up of at least ten monosaccharaides or their derivatives, linked by glycosidic bonds either in linear or branched chains [1]. They are the most abundant organic material on earth as well as the most prevalent biopolymer. They are polymeric in nature, and they usually have an oxygen bridge linking the monosaccharide monomers. Their monosaccharide building blocks and glycosidic linkages are known to establish their backbone and the determination of their complexity and diversity [2].

In recent times, locally made beads from wheat baking flour, has gained much interest especially from local community artisans in Nigeria, as a money spinning venture. However, their patronage experiences drab due to some limitations associated with them. These are; (i) undesirable light weight (ii) fragility problem (iii) poor fastness property (iv) irregular and rough surfaces and (v) compromised water resistibility. In the process of improving on the limitations, Idibie and co-worker synthesized a superior bead of wheat flour polysaccharide using composite material of titanium dioxide. Hence this study has undertaken to study the reaction mechanism and kinetics of the titaniumation of wheat flour polysaccharide.

The kinetics study of degradation of the minor neutral carbohydrates (composed of arabinosyl, galactosyl and mannosyl residuals) and uronic acid moieties of the agrofibre crop *Arundo donax* L. (giant reed) under conditions of ethanol-alkali delignification was under studied based on the properties of multi-component reaction system, and the result was accurately described in terms of two simultaneous irreversible first-order reactions, corresponding to two kinetically homogeneous polysaccharide fractions [3]. Literature also revealed that the kinetics study of the water extraction of foxtail millet polysaccharides, obeyed the first-order model [4]. This was based on the changes in polysaccharides mass concentration in the extract liquor. In this same vein, however, the kinetics of oxidation of pectin polysaccharide as a natural polymer by permanganate ion in aqueous perchloric acid was investigated spectrophotometrically, and the results showed that the initial rates was a first-order kinetics in respect of permanganate ion and fractional-order with respect to pectin polysaccharide [5]. The kinetics on the swelling of acrylamide grafted polysaccharides blend hydrogel was nevertheless found to obey first-order kinetic [6].

In this present study, the reaction mechanism of the substitution of titanium in the wheat polysaccharide molecules was investigated as well as using a modified Reductor Technique to study the kinetics of the chemical interaction between the wheat polysaccharide and the titanium dioxide.

2. Materials and Methods

Materials used for this study include the following: commercial wheat flour, titanium dioxide, cascamite glue and colorant which were locally obtained from Pyrex – IG Science Company Limited, Benin City, Edo State, Nigeria. While zinc amalgam, zinc, mercuric-chloride, sulfuric acid, potassium permanganate, ferric ammonium sulfate were obtained from Steve Nicholas and Charlec Chemicals and Disposables Ltd, Nigeria. Other materials used were suction flask, Jones reductor tube etc.

3. Preparation of the Dough/Bead

A known amount (50 g) of titanium dioxide was introduced into a bowl containing 300 ml water that was initially mixed with hydrogen peroxide. The presence of the hydrogen peroxide was to catalyze the solubilization of the titanium dioxide in water. This was followed with the addition of a known weight (50 g) of wheat flour and the entire mixture was vigorously stirred for uniformity. After this, adhesive and colorant were added with a controlled amount of water that was added gradually and stirred thoroughly to a smooth, non-sticky consistency dough. Thereafter, the dough was kneaded for 10 – 15 mins, and shaped into a known length and size and allowed to dry at room temperature for 24 hrs to form beads. The procedure was repeated at different temperatures (23 – 70^{o}C).

4. Kinetics Study

The kinetic study of the titanuimation of the wheat polysaccharide was carried out volumetrically according to a standard modified reductor technique (USP 36: 5406). Here, zinc amalgam column was prepared by adding 20 - to 30-mesh zinc to mercuric – chloride solution, by using 95 ml of the solution for each 100 g of zinc. After 10 mins, the solution was decanted from the zinc and the zinc was washed via decantation. Also, the zinc amalgam column was washed with 100 ml portion of 2 N sulfuric acid until 100 ml of the washing could not decolorize 1 drop of 0.1 N potassium permanganate. Following this, 50 ml ferric ammonium sulfate TS was placed in a 1000 ml suction flask with the addition of 0.1 N potassium permanganate until a faint pink colour persisted for 5 mins. The Jones reductor tube was attached to the neck of the flask, and 50 ml 2 N sulfuric acid was passed through the reductor at a rate of 30 ml/min. This was followed by passing the titaniumated sample solution of the different initial concentrations of TiO_2 through the reductor at the same rate, but with the addition of 100 ml each 2 N sulfuric acid and water. During the course of the experiment, the reductor was kept filled with water above the upper level of the amalgam. Taking cognizance against atmospheric oxygen interference, the suction was gradually released, and the solution was obtained in the receiver and titrated immediately with the titrant (0.1 N potassium permanganate VS) after a blank titration, and readings were recorded.

Percentage of titanium determined was thus calculated using Equation 1

$$\% \text{ Ti} = \left\{\frac{(V_s - V_B) \times N \times F}{W}\right\} \times 100 = \text{DT} \quad (1)$$

where: DT = Degree of titaniumation; V_s = titrant volume consumed by the sample (ml); V_b = Titrant volume consumed by the blank (ml); N = Actual normality of the titrant (mEq/mEq); W = Sample weight (mg); F = Equivalent factor, 79.88 mg/mEq.

5. Results and Discussion

The chemical interaction of the wheat polysaccharide (WP) in H_2O/H_2O_2 medium as shown in Figure 2 resulted in the titaniumation of the wheat polysaccharide molecule, and as the reaction time progressed the degree of titaniumation increased, as shown in Figure 3:

Figure-2. Titanuimation of wheat polysaccharide using titanium dioxide

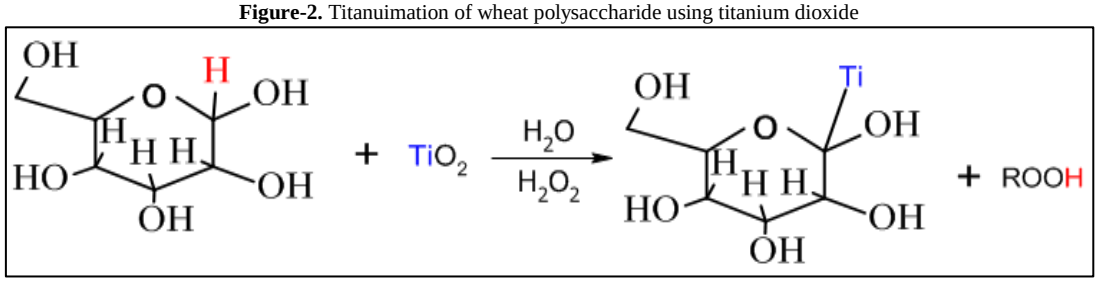
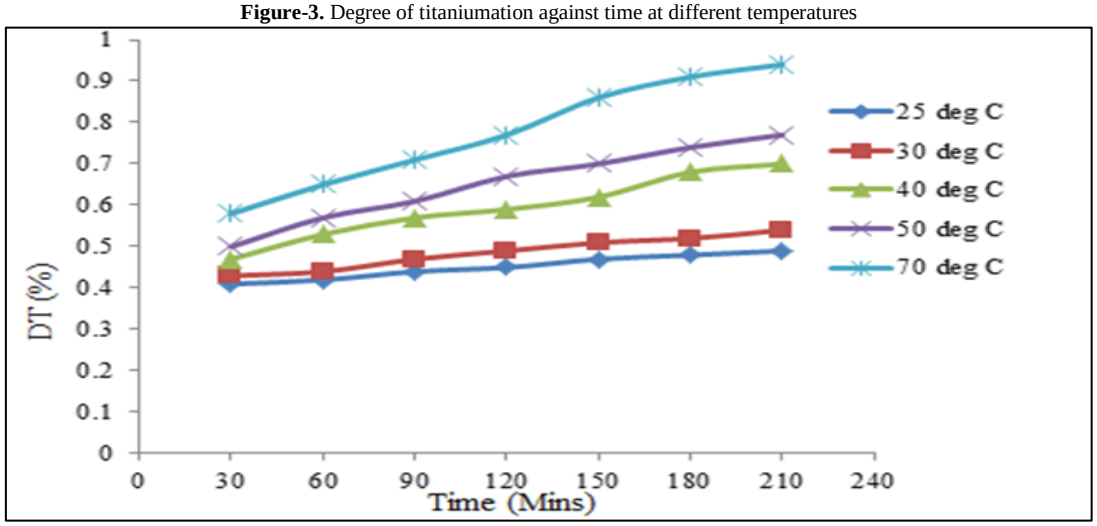


Figure-3. Degree of titaniumation against time at different temperatures



For emphasis on Figure 3, at 25^{o}C, DT increased from 0.41 % to 0.49 % and while at higher temperature of 70^{o}C, DT increased from 0.58 to 0.94 % as time progressed from 30 to 210 mins, respectively, while keeping both amount of WP and TiO_2 constant. Thus >1.9-fold was achieved between the two lower and upper range temperatures. This also implies that the titaniumation of wheat polysaccharide using TiO_2 is favourable at elevated temperature, hence DT increased with increasing temperature. However, effort to work beyond 70^{o}C could not enhance the degree of titaniumation, which could be due to saturation of sites of attachment and molecular breakdown of the polyasaccharide chain, as DT decreased in some of the attempts.

The reaction mechanism in reference to Figure 2 is such that an electrophile replaces a functional group in the ortho position of the compound (the replaced functional group is typically a hydrogen atom). Titanium dioxide is acting as the electrophile and has high affinity for hydrogen, while the oxygen atoms of TiO_2 have much stronger electronegativity than the titanium atom, and the shared electrons density are closer to the oxygen atoms, which gives the titanium atom a positive charge while the oxygen a negative charge. In the presence of H_2O, however, TiO_2 is insoluble in water and requires the addition of hydrogen perioxide (H_2O_2) to be solubilized in water. Hence when in any reaction a stronger electrophile substitutes or replaces a comparatively weaker electrophile, then the reaction is termed as "Electrophilic Substitution Reaction". Therefore, the titaniumation of the glucose monomer is an electrophilic substitution reaction. Based on this, the kinetic model of the electrophilic substitution of the titaniumation of the wheat polysaccharide is assumed.

6. Kinetic Model

In order to come up with a kinetic model for the titaniumation of WP, the following assumptions were made. These include:

1) The titaniumatiom reaction occurs in each repeat unit of the polysaccharide.
2) The electrophilic attack and substitution favours the ortho position of the ring.
3) The reaction is assumed to be first order in respect to the polysaccharide.
4) The reaction occurring is represented in Figure 2 above.
5) Change in volume is not applicable.
6) The initial concentration of titanium dioxide is much higher than that of each of the repeat unit of the polysaccharide.
7) Possible effect of ROOH as a by-product on the reaction is neglected.
8) The degree of titaniumation is equal to the percentage of titanium present in the polysaccharide.

Therefore, for simplicity, Figure 2 above can be represented as:

$$a + b \rightarrow c + d \quad (1)$$

where: a = repeating unit of the polysaccharide, b = titanium dioxide, c = titaniumated polysaccharide and d = organic acid.

Defining concentrations at different times, we have:

at $t = 0$

it is the initial concentration of the polysaccharide = C_{a0}

while the initial concentration of titanium dioxide = C_{b0}
the initial concentration of titaniumated polysaccharide = 0
and
at $t = t$:
the concentration of polysaccharide
$= C_a = C_{ao} - C_c$
the concentration of titanium dioxide
$= C_b = C_{b0} - C_c$
and the concentration of titaniumated polysaccharide
$= C_c$

Based on the assumption (3) that the titaniumation of the WP is a first order, the rate equation follows [7]:

$$r_a = \frac{dC_a}{dt} = -k_1 C_a C_b \quad (2)$$

where: k_1 = first order rate constant with respect to the polysaccharide concentration being the substrate.

Since the initial concentration of titanium dioxide is much higher than that of each of the repeat unit of the polysaccharide according to the 6th assumption, this implies that

$C_b0 >> C_a0 > C_c$
and so
$(C_b0 - C_c) \approx C_bo$
Thus Equation (2) reduces to:

$$\frac{dC_a}{C_a} = -k_1 C_{b0} dt \quad (3)$$

Integrating Equation (3) and taking limits; C = Ca0 (t = t0) to C = C_a (t = t), we have

$$ln\left(\frac{C_a}{C_{a0}}\right) = k_1 C_{b0} t \quad (4)$$

Taking assumption 8 into consideration, then

$$DT = \frac{C_{a0} - C_a}{C_{a0}} = \frac{C_{a0}}{C_{a0}} - \frac{C_a}{C_{a0}} = 1 - \frac{C_a}{C_{a0}} \quad (5)$$

Therefore, substituting Equation (5) into Equation (4), gives the modified first order kinetic as Equation (6):

$$ln(1 - DT) = -k_1 C_{b0} t \quad (6)$$

Therefore, Equation (6) is the kinetic model for the titaniumation of the wheat polysaccharide in H_2O/H_2O_2 medium.

The rate constant k_1 at each reaction temperature was obtained via linearization of Equation (6) to be:

$$-ln\,(1 - DT) = k_1 C_{b0} t \quad (7)$$

And a plot of $-ln\,(1 - DT)$ against *time* at different temperatures considered as shown in Figure 4 was used to obtain the reaction rate constant (k_1) at different temperatures. Table 1 presents the various k_1, different operating temperatures as well as their coefficient of correlation (R^2). The table showed a consistency of k_1 which implies that the titaniumation of the wheat polysaccharide obeyed the first order kinetics and which was corroborated with the high R^2 values as shown in Table 1 as well.

Figure-4. A plot of –ln (–DT) vs titaniumation time at different temperatures

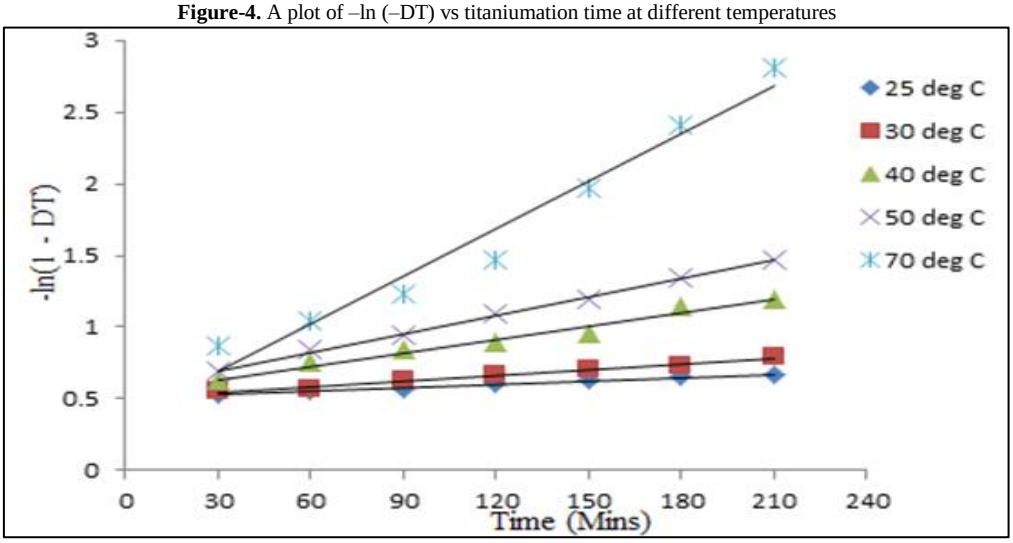


Table-1. Reaction rate constant and coefficient of correlation at varying temperatures

Operating Temperature (^oC)	Reaction rate constant (k_1)	Coefficient of correlation (R^2)
25	0.001	0.992
30	0.002	0.982
40	0.003	0.977
50	0.004	0.098
70	0.011	0.963

The obtained values of the reaction rate constant as presented in Table 1 was used to determine the activation energy and reaction coefficient via Arrhenius equation:

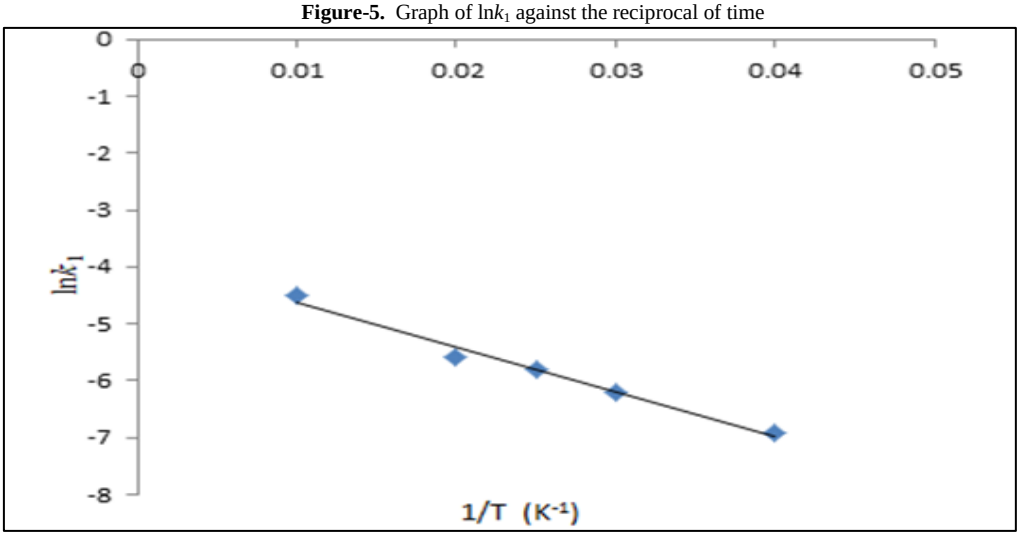
$$k = k_0 e^{-\frac{E_a}{RT}} \quad (8)$$

Re-arranging Equation (8), we have:

$$lnk = lnk_0 - \frac{E_a}{RT} \quad (9)$$

The slope and vertical intercept of lnk_1 against the reciprocal of *time* as shown in Figure 5 are equal to $-\frac{E_a}{RT}$ and lnk_0, respectively. As a result, the activation energy (E_a) and reaction rate coefficient (k_0) became 178.64 kJ/mol and 1.34 g/mol, respectively.

Figure-5. Graph of lnk_1 against the reciprocal of time



7. Conclusion

Investigation into the reaction mechanism and kinetics of wheat polysaccharide using titanium dioxide in H_2O/H_2O_2 medium in bead making process showed that the titaniumation of the polysaccharide molecules followed an electrophilic substitution reaction in which a ring is titaniumated at a time. The reaction was found to be favoured at elevated temperature and, it obeyed a first order kinetics model. However, the activation energy (E_a) and reaction rate coefficient (k_0) were 178.64 kJ/mol and 1.34 g/mol, respectively.

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