

Destruction of Amylopectin in the Presence and Absence of TiO₂ Nanoparticles

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ABSTRACT

Today, the use of natural polymers and their replacement with synthetic polymers in various fields of science has attracted much attention. Reducing the associated risks, easy access, and being cost-effective are among the advantages of using natural polymers compared to the synthetic polymers. In this research, the destruction of amylopectin in the presence and absence of titanium dioxide nanoparticles was investigated. The main objectives of this research include the replacement of the synthetic polymer materials with natural polymeric materials in order to produce new raw materials with high performance and less pollution to be used in various fields of science, particularly pharmaceuticals and medicine, and also studying its destructive properties. A comparison of the analysis methods besides adding titanium dioxide and other chemical additives would provide a variety of possible modes to study on the properties of this polymer. To investigate the viscosity of experimental solutions, the techniques such as XRD and FT-IR were used to detect the degradation rate of the samples.

Keywords: Amylopectin; Titanium dioxide; Nanoparticles

1. INTRODUCTION

Starch granules contain two large polyglucans, namely branched amylopectin and essentially linear amylose. In all non-permanent starches, amylopectin is the main ingredient responsible for the internal structure of starch granules, which is a native and semi-crystalline starch [1]. Amylopectin is generally accepted as a layered -structure constructor, but the nature of the blocks is only soluble.

Amylopectin contains numerous chains of glucosyl units divided into short and long chains. These chains are clustered using endo enzymes [2]. The length of the amylopectin chain is precise and influences the physico-chemical properties of starch determining the starch capability [3]. Polygonal and solid starches have mono-phase degradation patterns during hydrolysis, and solid starch has a higher

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resistance to hydrolysis than starch polygon. However, long and hollow starches are quickly decomposed in the early stages of hydrolysis, but have high degradation resistance based on the two-phase hydrolysis pattern in the next period [4]. Amylopectin is usually known as the main starch compound, as the ratio of amylopectin to amylose is usually 3:1 or 75 to 25% [5]. Natural polysaccharides such as starch amylopectin are widely used in the food and paper industries, industrial applications, and biodegradable plastics industries [6]. A successful gene therapy is dependent on cell proliferation in high gene transfer carriers and cellular toxicity [7]. Non-viral gene carriers, especially cationic polymers are commonly used in gene therapy [8]. Unlike viral carriers, these carriers have numerous advantages such as lower immune responses, the ability to carry large DNA molecules, production at low prices and in large quantities. The structure of cationic polymers with DNA molecules produces portable and stable complexes [9]. Natural polysaccharides such as amylopectin are considered as non-toxic, biocompatible, and biodegradable in the field of biomaterials [9]. Because of these positive points, polyacetons based on multi-branch polysaccharides have been developed as a new form of non-viral carriers [10]. Amylopectin hydroxyl groups are very active for simple reactions such as amination. Amylopectin conjugated with a variety of oligoamines can be used as a kind of non-viral carriers [11]. TiO_2 nanoparticles have exhibited good electrical, optical, and photocatalytic properties. TiO_2 application and performance are heavily influenced by the crystalline structure, shape, and size of its particles [12]. Therefore, much effort has been made to produce TiO_2 NPs of controlled size, shape, and porosity in order to be used in thin layers of ceramics,

composites, and catalysts [13]. Moreover, TiO_2 is one of the most important raw materials widely used for producing the paints, plastics, cosmetics, papers, and sensors. In many cases TiO_3 is produced by the process of sulfate or chloride, but the produced particles are relatively coarse in the micron range [14]. Several methods have been used to synthesize TiO_3 nanoparticles including the hydrolysis method the sol-gel method on a carbon-activated substrate Hydrothermal method under heat and pressure microwave hydrothermal method and chemical method [15-18].

2. METHODS

2.1. *TiO₂ Enzymatic Degradation of Amylopectin in the Presence of a Nanoparticle Catalyst*

A solution of amylopectin with a concentration of L / 01g was mixed with 1 mol of NaOH solution to prepare 1mg of alpha- TiO_3 amylase enzyme, and then different amounts of nanoparticles were added (0.1 to 0.5 gr) by magnetic stirrer at certain times. Then, the centrifugation was used to dissolve the catalysts from the solutions after finishing the reaction. For this purpose, the selected samples were centrifuged at three stages for 2 min at the top of the centrifuge, and the solution was used for viscosity investigations.

3. RESULTS AND DISCUSSION

3.1. *Enzymatic Degradation of Amylopectin in the Presence of Tio₂ Nanoparticles*

In this section, the enzymatic degradation of amylopectin is discussed in the presence of TiO_2 nanoparticles using a solvent of NaOH.

3.2. *Enzymatic Degradation of Amylopectin in a Solvent of NaOH*

To investigate the enzymatic degradation of amylopectin in a solvent, a molar of

NaOH with a sample density of 10g/l of amylopectin was added to different values of TiO₂ nanoparticles with a mass of 0/01 to 0/05, and was examined in different times, and then the effect of catalyzer increment of TiO₂ nanoparticles was investigated on the relative viscosity. Figure 1 shows the changes in the relative viscosity for degradation of samples in different times.

3.3. Comparison of the Effects of Amylopectin Degradation in the Presence and Absence of TIO₂ Nanoparticles

Figure 2 shows the comparison of the destruction process in the presence and absence of titanium dioxide nanoparticles.

The results showed that, the depletion rate is lower in the presence of TiO₂ nanoparticles.

Given the catalyst effect, it can be concluded that, the higher the catalyst concentration, the degradation rate will be reduced.

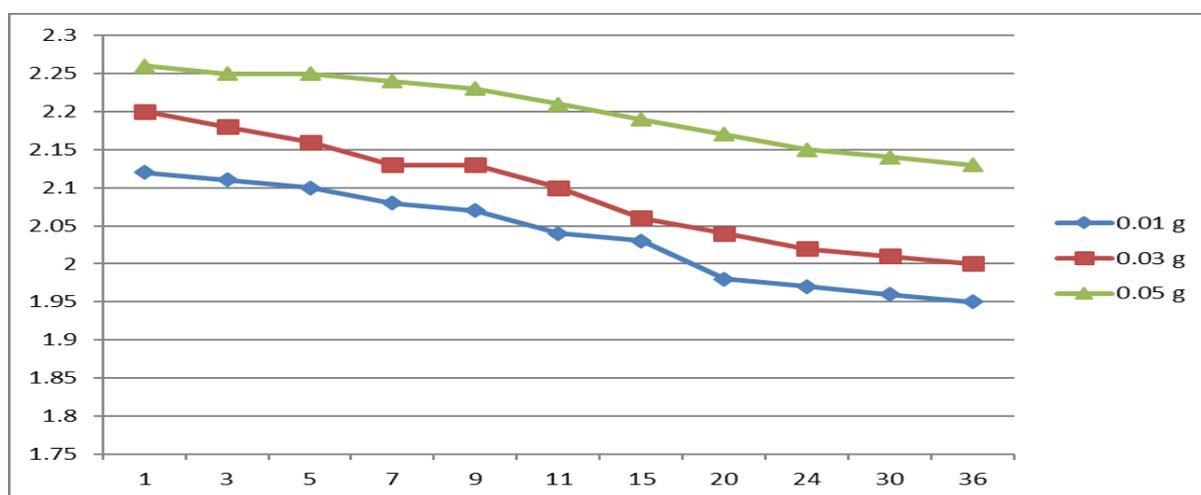


Fig. 1. Changes in the relative viscosity for amylopectin in terms of different reaction times for different concentrations of nanoparticles at a temperature of 25 ° C using NaOH solvent

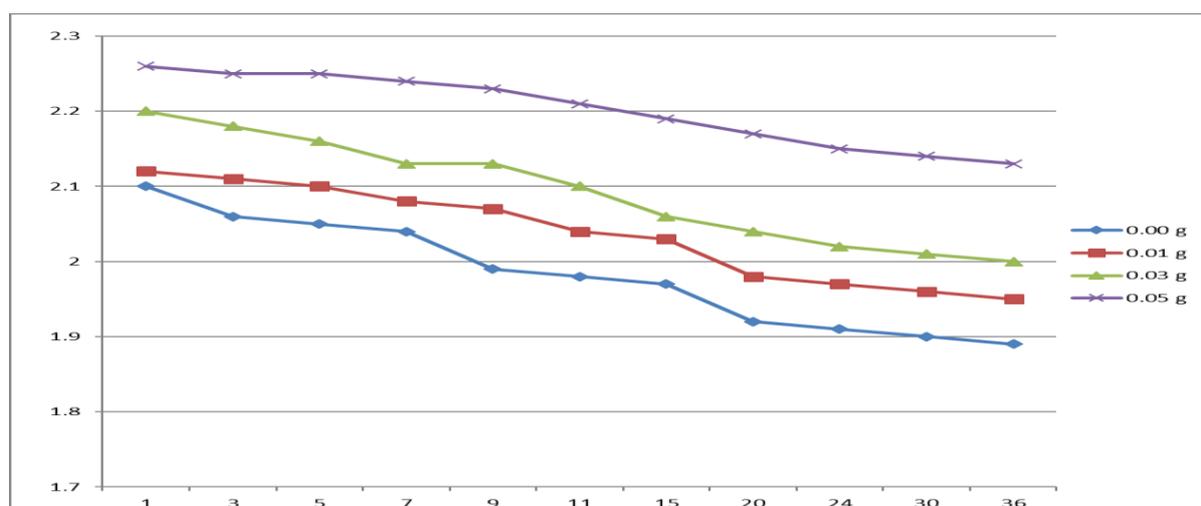


Fig. 2. Changes in the relative viscosity for amylopectin in terms of different reaction times for different concentrations of nanoparticles at 32 ° C using NaOH solvent.

3.4. Kinetics Model

In this model, the polymer degradation rate is defined as the number of moles broken in one liter and at the time unit. It should be noted that, by breaking a polymer chain, two polymer chains are formed with low molecular mass. Therefore, the destruction rate is written as follows:

$$k' = (1-n) \left[\frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}} \right]^{(1-n)/\alpha} k$$

3.5. FT - IR Spectroscopy

The IR-FT spectra of the sample are shown in Figures 3, 4, and 5 in the presence of different concentrations of nano TiO₂ in a NaOH solvent. In a sample of TiO₂ nanoparticles, by increasing the weight gain of titanium dioxide, the OH-tensile vibrations increased, indicating the decrease in the degradability. This means that, the presence of nanoparticles results in the polymer stability.

Table 1. The apparent velocity constants obtained in terms of time and constant velocity calculated for the degradation reaction for various concentrations (mol 1.72, L.-1.72, S.-1) at 25 °C using NaOH solvent By increasing the concentrations, the constant speed of the degradation process reduced.

Concentration (g.lit ⁻¹)	$k' \times 10^3$	$k \times 10^5$
10	3.3	1.65
15	2.4	1.30
20	2.2	1.02

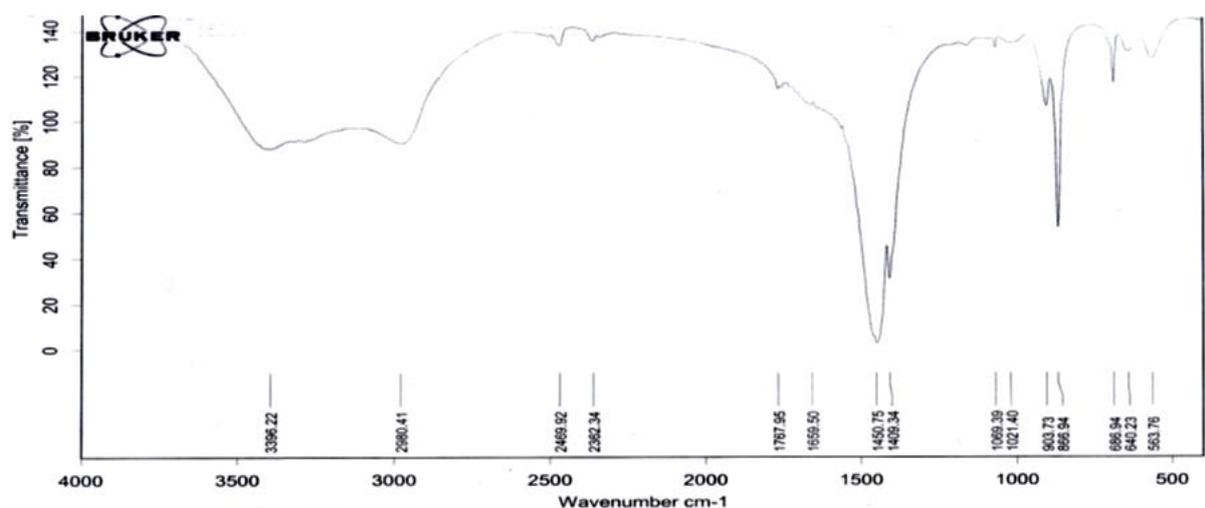


Fig. 3. FT- IR spectrum of amylopectin enzyme degradation in the presence of 1% TiO₂ nanoparticles in a NaOH solvent.

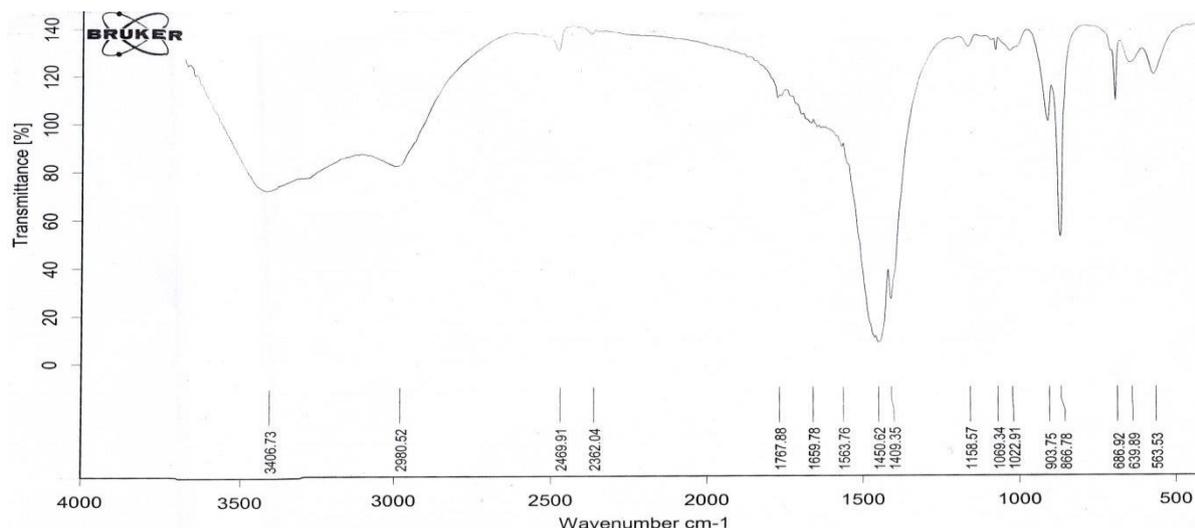


Fig. 4. FT- IR spectrum of amylopectin enzyme degradation in the presence of 3% TiO_2 nanoparticles in a NaOH solvent.

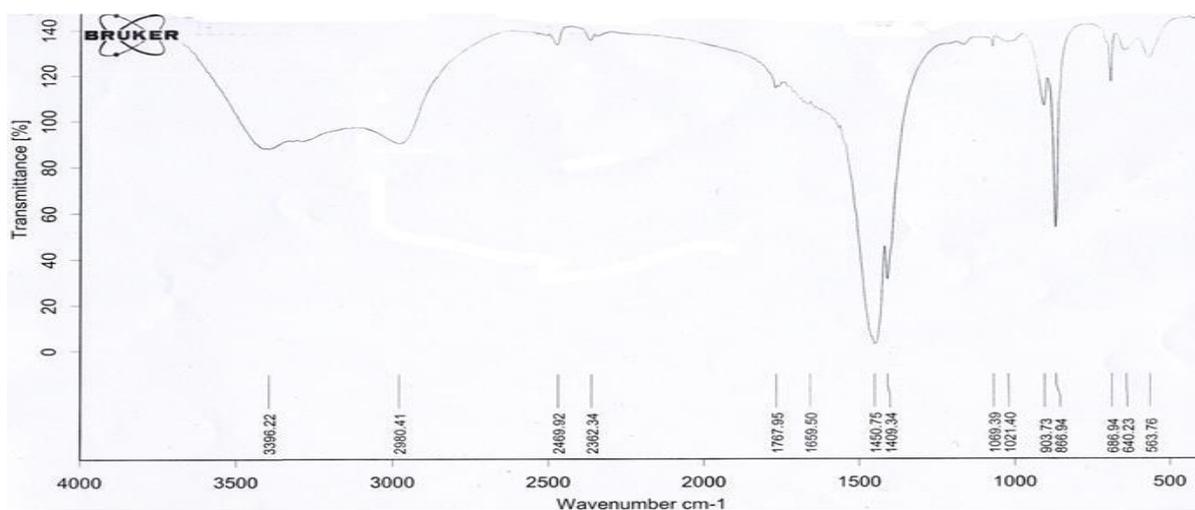


Fig. 5. FT- IR spectrum of amylopectin enzyme degradation in the presence of 5% TiO_2 nanoparticles in a NaOH solvent.

The FT- IR spectrum presented in Figures 2, 3, 4, and 5 showed that, the destruction was in the direction of the separation of the monomers from each other rather than the destruction of the ring itself, because the peak of the ring vibrations did not change significantly. However, after degradation of the enzyme in the courier, it was observed that, OH-tensile vibrations resulted from the separation of the monomers and the presence of the hydroxyl groups in the ring. However, in a sample of TiO_3

nanoparticle, an increase was observed in the OH-tensile vibration peak, resulting in lower polymer stability and less degradation.

3.6. Analysis of the Samples Using the XRD¹ Technique

The X-ray area in the electromagnetic spectrum is in the range between the beam of γ and ultraviolet radiation. Using this spectral region, the information can be

¹ X-Ray Diffraction

obtained about the structure and nature of the material (kasai et al., 2005). The X-ray diffraction technique is used to describe the nanoparticles in the following cases:

A) The general shape of the spectrum and angles appearing in the peaks represent the nature and crystalline structure of the nanoparticles.

B) From the integral intensity of the couriers, one can find the percentage of species found in the sample.

C) Another application of the XRD spectrum is calculating the approximate size of the nanoparticles. When the particle size is smaller than 100 nm, the XRD spectra peak becomes considerably wider; this factor can be used to estimate the size of the nanoparticles. For this purpose, the Scherrer relation is used.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

In this case, D is the diameter of the particle in terms of angstrom, λ is the wavelength of the X-rays used in Angstrom, β is the width of the strongest peak of the corresponding species in half its height in radians, and θ is the angle at which the peak appears.

The XRD spectrum obtained from the analysis of TiO₂ nanoparticles is shown in Fig. 6. As shown in Fig 6, the strongest peak was observed at $2\theta = 27/38$, with a peak width of 0/0072 radians in half its height.

The wavelength used was 1/5478 Angstrom. The average size of the nanoparticles was calculated using a 19-nm Sherrer equation.

In this section, the spectra obtained from the analysis of the samples at different stages of study and the different conditions applied to the destruction of amylopectin using X-Ray Diffraction (XRD) are presented. The XRD technique provides useful information about the

crystallinity of materials. The degree of crystallinity of starch has already been studied, and the crystalline structure of amylopectin has been proven (Cubao et al., 2008).

In a particular kind of starch known as Chalky starch¹ where the amylopectin ratio is very dominant in amylose, XRD analyses show more regular crystalline structure (Patindol et al., 2003).

Figure 2 shows the XRD spectrum pattern for pure and undiluted amylopectin. As shown in Fig 2, six distinct peaks were visible for crystalline regions in the original amylopectin digraph. However, the degree of crystallinity was low, and the peaks of this state included amylopectin in $2\theta=15$ and $2\theta=35$, consistent with the pattern provided in the study by Shi² et al. (Shi. et al., 1998).

Figures 8, 9, and 10 represent the XRD spectrum pattern of a demineralized sample of amylopectin in the presence of different concentrations of rutile titanium dioxide nanoparticles. Comparison of the shapes showed that, by increasing the nanoparticle size, the peak of the corresponding peak height increased in $2\theta=15$, and less degradation was observed. This means that, the amount of crystallization of amylopectin molecules increased due to the degradation.

CONCLUSION

The results of the present study revealed that, the higher the concentration percentage of rutile titanium dioxide nanoparticles, the degradation rate will be reduced and The X-ray diffraction spectrum also showed that, as a result of degradation, the physical structure of amylopectin molecules varies from crystalline to superficial. FT- IR

¹ Chalky starch

² Shi

spectroscopy results showed the effective degradation of the polymer.

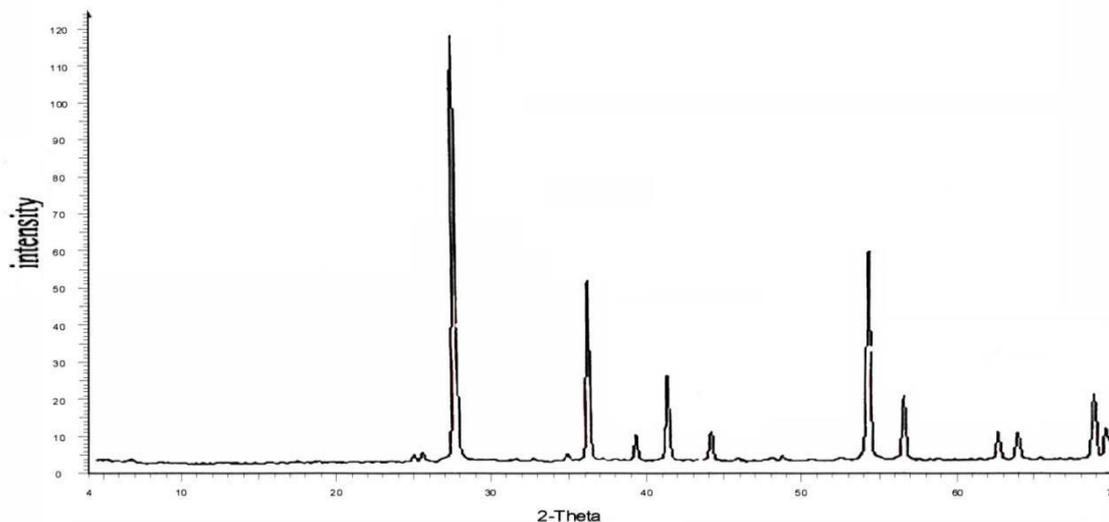


Fig. 6. XRD spectrum of rutile titanium dioxide nano particles.

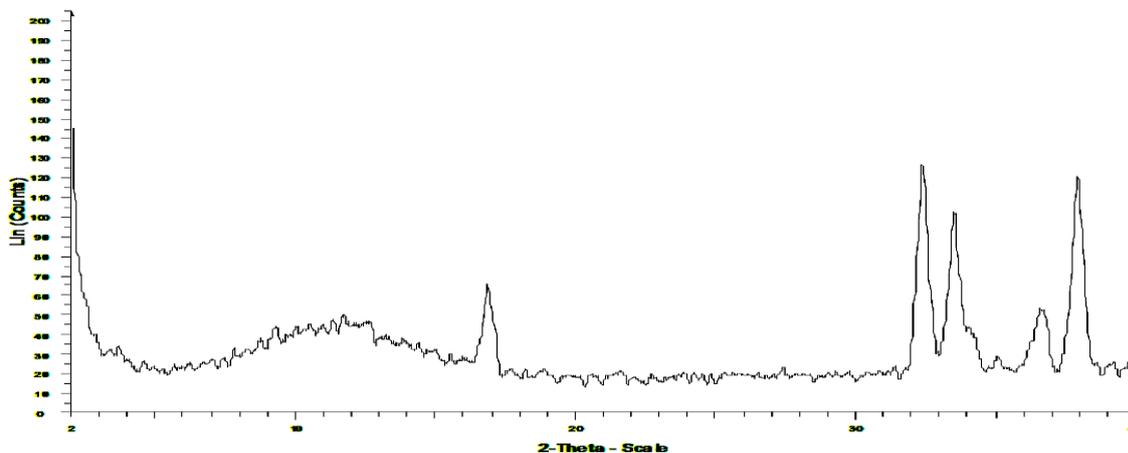


Fig. 7. Primary XRD diffraction pattern of amylopectin.

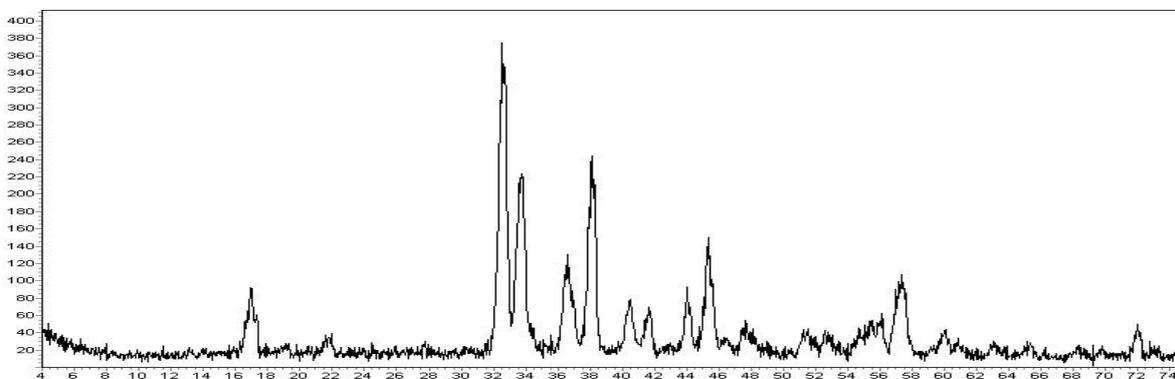


Fig. 8. XRD pattern destroyed in the presence of 1 % titanium dioxide nanoparticles.

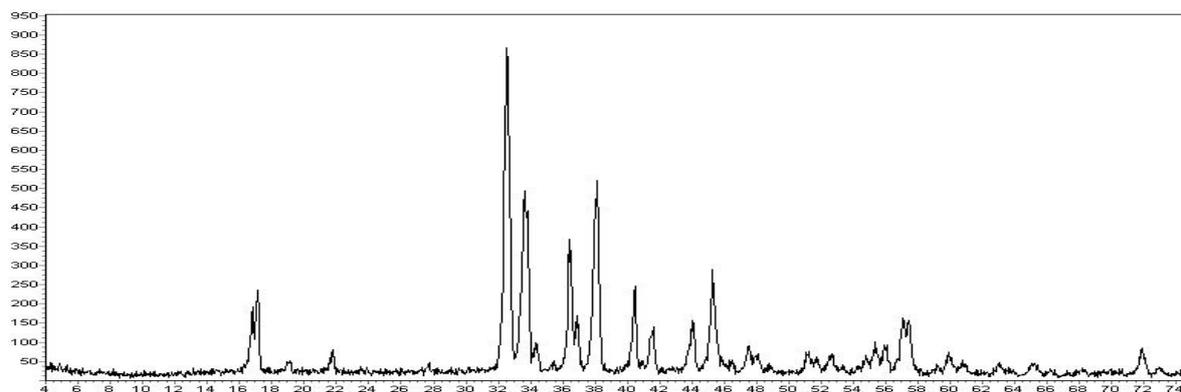


Fig. 9. XRD pattern destroyed in the presence of 3 % titanium dioxide nanoparticles.

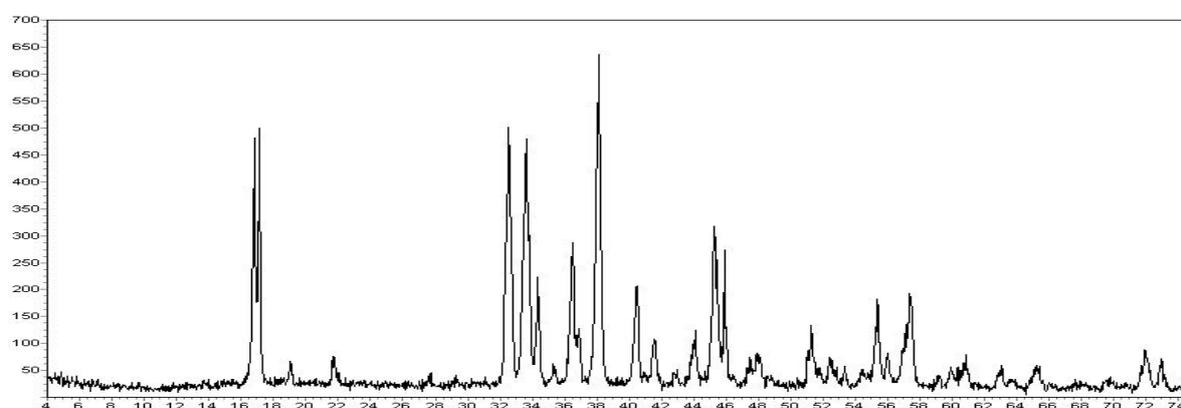


Fig. 10. XRD pattern destroyed in the presence of 5 % titanium dioxide nanoparticles.

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