Photocatalytic digestion of total phosphorus utilising nanotitanium dioxide photocatalyst

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Thermal-assisted ultraviolet (UV) and H_2O_2-assisted UV photocatalytic oxidation methods utilizing nano-TiO_2 photocatalyst are presented for the digestion of total phosphorus (TP) in water. The photocatalytic experiments for TP digestion were conducted using a 365 nm wavelength UV light, and TiO_2 nanoparticles immobilized on a silicon wafer as the photocatalyst. The effects of H_2O_2 and temperature on the UV photocatalytic oxidation process are explained. The pseudo-first-order rate constants k of two phosphorus compounds for the UV digestion processes were obtained according to the pseudo-first-order equation. Both H_2O_2 and heating could improve the efficiency of the UV photocatalytic oxidation method. But by comparison, the enhancement of heating on the UV photocatalysis process is more distinctly than H_2O_2. In addition, the thermal-assisted UV digestion process will not lead to secondary pollution since no oxidant is needed in this digestion process, which makes it more compatible with electrochemical detection of TP. The thermal-assisted UV digestion method was employed for the digestion of real water samples. Compared with the conventional thermal digestion method for TP detection, this thermal-assisted UV digestion process decreased the digestion temperature from 120°C to 60°C within the same time, which enable the digestion process work at normal pressure.

1. Introduction: Total phosphorus (TP) is the sum of orthophosphates, condensed phosphates and organically bound phosphorus [1]. Phosphorus determination is of great importance from the environmental and nutritional point of view since total phosphorus is used for predicting algal biomass [2]. The analysis of TP in water samples (natural, waste etc.) is especially complex owing to the fact that phosphorus exists in both inorganic and organic forms. Before the detection of TP, a digestion pretreatment procedure of the water sample must be conducted to convert all types of phosphorus to orthophosphate. Subsequently, either the electrochemical or the optical inspection method is employed to detect the concentration of orthophosphates and complete the detection of TP.

The traditional method for TP digestion is high temperature oxidation (HTO) with a temperature of 120°C and a pressure of 1.1 kg/cm², which is high power consuming. Potassium persulphate is often used as the oxidant agent in this traditional digestion process [3, 4]. Photocatalysis has recently appeared as a new emerging technique with the advantages of having high efficiency and being environmentally friendly. Titanium dioxide (TiO_2) has often been proposed for the elimination of organic pollutants, because of the merits of relatively inexpensive, safe, chemically stable and high photocatalytic activity [5]. Ultraviolet (UV) light with energy equal to or higher than the corresponding bandgap irradiate at the TiO_2, hole/electron pairs (e^-/h^+) could be generated [6]. The photogenerated holes react with either H_2O or OH^- to generate hydroxyl radicals (·OH) which are strong oxidants, as shown in the following equations:

$$TiO_2 + hv \rightarrow TiO_2(e^- + h^+) \tag{1}$$

$$h^+ + H_2O \rightarrow H^+ + \cdot OH \tag{2}$$

$$h^+ + OH^- \rightarrow \cdot OH \tag{3}$$
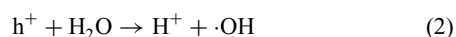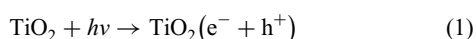
Excited state conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat and get trapped in surface states or carrier traps [7]. However, because of the short lifetime of photogenerated carriers, the efficiency of the UV photocatalysis process is relatively low. Hence, oxidants, such as H_2O_2, are often employed to inhibit the electron–hole recombination in many UV degradation processes of organic pollutants [5, 7–9].

Usually, the UV photocatalytic oxidation process is conducted at room temperature. To improve the efficiency, a thermal-assisted UV oxidation method is presented in this Letter. Both thermal-assisted UV and H_2O_2-assisted UV photocatalytic oxidation methods were employed for the digestion of total phosphorus. A 365 nm wavelength UV light was used as the UV light source and the commercially available TiO_2 nanoparticles, immobilised on a silicon wafer, were used as the catalyst. Sodium tripolyphosphate ($Na_5P_3O_{10}$) and sodium glycerophosphate ($C_3H_7Na_2O_6P$) were used as the typical substance of TP to conduct the digestion experiments. The H_2O_2-assisted UV digestion process was conducted at different concentrations of H_2O_2 and the thermal-assisted UV digestion process was conducted at different temperatures. The working mechanisms of both these two digestion methods are also discussed in this Letter. Compared with the traditional UV photocatalytic oxidation process, both the thermal-assisted UV and H_2O_2-assisted UV oxidation methods could increase the efficiency. Compared with the conventional thermal digestion method for TP detection, the thermal-assisted UV digestion method decreases the digestion temperature, which enables the digestion process to work at normal pressure.

2. Experiments
2.1. Materials and equipments: $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ (Beijing Chemical Reagent Company, China) were used to prepare the test solutions and the initial concentrations of $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ solution used as the test solution were 4 mg/l (by weight of P), respectively. Hydrogen peroxide (H_2O_2, Beijing Chemical Reagent Company, China) was used as the electron acceptor for the UV photocatalysis process. Ascorbic acid ($C_6H_8O_6$), ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O)$], potassium antimony tartrate ($KSbC_4H_4O_7 \cdot 1/2H_2O$) and H_2SO_4 (Beijing Chemical Reagent Company, China) were used to prepare

the colour reagent for the digested water samples. Commercial TiO_2 nanoparticles were purchased from Yunnan University (China), and used without further treatment after purchase. The test solutions were all used without pH adjustment. The initial pH values for $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ with the concentration of 4 mg/l were 7.9 and 8.2, respectively.

The UV light was supplied by a middle-pressure lamp (SB-100P/F/J from Brightstars Corporation, China); a hotplate (KW-4AH from Chemat Technology Corporation, China) was used as the heating equipment; and a UV spectrophotometer (Biospec-nano from Shimadiu Corporation, Japan) was employed to measure the concentration of orthophosphate.

2.2. Preparation of TiO_2: TiO_2 film on a silicon wafer (TiO_2/silicon) was prepared by spin-coating of glue and dispersing of TiO_2 particles on the silicon wafer. The diameter of the silicon wafer was 2 inches. A 300 nm-thick silicon dioxide layer was made by thermal oxidation. First, epoxide-resin glue was spun on the surface of the wafer, with a spin rate of 2000 rpm for 1 min. Then, 0.05 g TiO_2 nanoparticles were dispersed on the surface of the glue. The TiO_2/silicon was then dried at 100°C for 2 h.

2.3. Measurement: The digestion process of the water sample was started by immersing the TiO_2 nanoparticles-attached silicon chip into the cylinder reactor, and then the UV light and heater were turned on. Three reactors (one for blank control and another two for the water samples) were placed on the heater under the UV lamp. The radiated power of UV light on the surface of the chip was 7000 μW/cm². The temperature of the reaction was controlled by the heater. The supported TiO_2 was used, repetitively, and the silicon wafers were washed with ultra-pure water for 1 min after each digestion process. After the digestion process, the solutions need to be cooled for 15 min, and then 1 ml of ascorbic acid solution and 1 ml of ammonium molybdate solution were added into the digested solution in order. This mixed solution was kept stable for 10 min after mixing thoroughly. The orthophosphate concentration (weight by P) of the digested solution was measured by the UV spectrophotometer at a wavelength of 700 nm against a reagent blank.

3. Results and discussion

3.1. X-ray diffraction (XRD) and scanning electron microscope (SEM) examination of TiO_2 film on the silicon wafer: XRD analysis was performed to identify the phase structure and composition of nanoTiO_2 powders, as shown in Fig. 1. The TiO_2 used in this work is a mixture of anatase and rutile (anatase: 84%, rutile: 16%). It has been reported that the mixture of anatase and rutile with a certain proportion has the best catalysis activity [10]. The reason could be that the mixture of two different crystal structures has a larger disfigurement density in
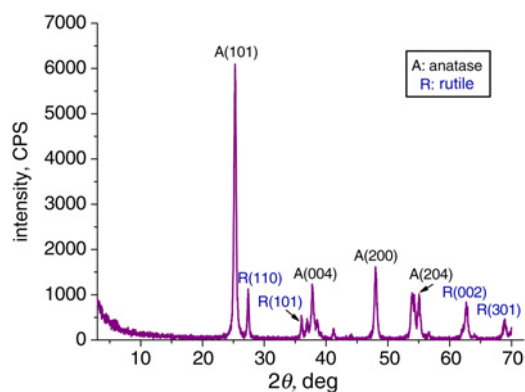
the crystal lattices, and the disfigurements form the carrier traps, in which the electron or hole could be trapped. In this way, the lifetimes of both the hole and the electron were extended. Fig. 2 shows the SEM image of nanoTiO_2 on the surface of the silicon wafer, the TiO_2 particles are distributed uniformly and the average size of the TiO_2 particle is about 50 nm.

3.2. UV photocatalytic digestion process
3.2.1 Individual UV photocatalytic digestion process: The individual photocatalytic digestion experiments (at room temperature, without H_2O_2) were conducted using initial concentration 4 mg/l (weight by P) $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$, respectively. Fig. 3 shows the conversion rates (the ratio of the concentration of P converted into orthophosphate to the initial concentration of P in phosphorus compound) of the two typical phosphorus substances for different irradiation times. The conversion rates elevated with the increase of the irradiation time for both substances, but not in a linear relationship. It was observed that the conversion rates increased rapidly during the first 30 min and then with the irradiation time increased, the acceleration of the conversion rate became slower and slower. After 120 min, the conversion rates of $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ could reach 78.8 and 92.6%, respectively.

3.2.2 H_2O_2-assisted UV photocatalytic digestion process: To improve the efficiency of the UV photocatalysis process, H_2O_2 was employed for the digestion of TP in water. The concentrations of the H_2O_2 used in this work were 247, 493, 740 and 987 mg/l. Fig. 4 shows the conversion rates at different reaction times and H_2O_2 concentrations. At a certain H_2O_2 concentration, the conversion rate increased with the increase of digestion time; at a certain digestion time, the conversion rates increased with the increase of
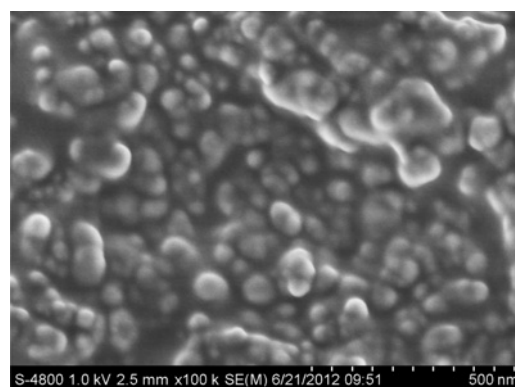
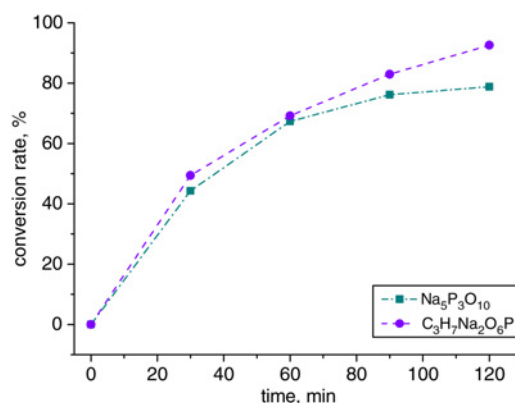**Figure 2** *SEM image of TiO_2 nanoparticles on surface of silicon wafer*

Figure 1 *XRD pattern of TiO_2 nanoparticles*

Figure 3 *Conversion rates of two typical phosphorus substances against irradiation time for the individual UV digestion process*
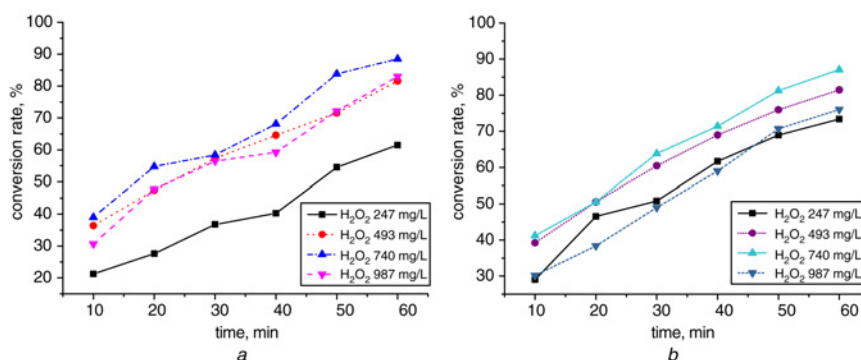
Figure 4 *Conversion rates of two typical phosphorus substances against irradiation time at different H_2O_2 concentrations*
a $Na_5P_3O_{10}$
b $C_3H_7Na_2O_6P$

the concentration of H_2O_2, but when the concentration of H_2O_2 was higher than 740 mg/l, the conversion rate decreased. At the condition of 60 min and 740 mg/l H_2O_2, the conversion rates of $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ were 88.5 and 87%, respectively.

Compared with the results of the individual UV digestion process, the enhancement of H_2O_2 on the UV photocatalytic digestion process could be observed. The UV photocatalytic oxidation relay on the strong characteristic of ·OH was formed by the reaction of h^+ and OH^- in water. The addition of H_2O_2 could not only extend the lifetime of holes for the consumption of e^- by H_2O_2, but also increase the formation rate of ·OH through the reduction of H_2O_2 by electrons. Besides, the UV radiation of H_2O_2 would also lead to the decomposition of H_2O_2 to produce ·OH. The process could be expressed as the following equations:

$$H_2O_2 + e^- \rightarrow ·OH + OH^- \tag{4}$$

$$H_2O_2 + hv \rightarrow 2 · OH \tag{5}$$

However, excessive H_2O_2 could react with ·OH, which led to the consumption of the strong oxidant ·OH, as shown in (6). Hence, when excessive H_2O_2 is added in the water sample, the conversion rate will decrease.

$$H_2O_2 + ·OH \rightarrow H_2O + ·HO_2 \tag{6}$$
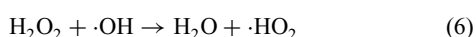
Therefore an optimum concentration of H_2O_2 is added to the water sample. When the concentration of H_2O_2 is lower than the optimum, increasing the concentration will improve the oxidation capability of UV photocatalysis. However, once the concentration of H_2O_2 is higher than the optimum value, increasing the H_2O_2 concentration will lead to the depression of UV photocatalysis capability. In this Letter, the optimum concentration of H_2O_2 was 740 mg/l.

3.2.3 Thermal-assisted UV photocatalytic digestion process: Thermal-assisted UV digestion experiments were conducted at reaction temperatures of 40, 50 and 60°C. Conversion rates of the two typical phosphorus substances at different irradiation times and different temperatures are shown in Fig. 5.

It can be seen that the change trends of the conversion rate against irradiation time at different reaction temperatures are similar to that at room temperature, and the conversion rates are larger at higher reaction temperatures than that at room temperature, which means that the oxidation rate of phosphorus compounds to orthophosphate is much faster at a higher reaction temperature. At the condition of 30 min and 60°C, the conversion rates of $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ are 95.9 and 97.3%, respectively.

From the results above, a significant enhanced effect of heating on the photocatalysis oxidation digestion process could be observed. In the collision theory, it is thought that the collision between reagents is the precondition for the reaction to occur. Among all the collisions, most of them could not produce a reaction, and only very minor collisions are effective [11]. First, molecules in the collisions that could react must have sufficient energy to overcome the repulsive force between electron clouds because of the infinite approach of the molecules. The minimum energy needed is called the activation energy E_a. In this way, the rearrangement of atoms in molecules could take place, which means that the chemical reaction occurs. Hence, for a chemical reaction to take place, the molecules must collide with the energies equal to or greater than the activation energy for the reaction. At
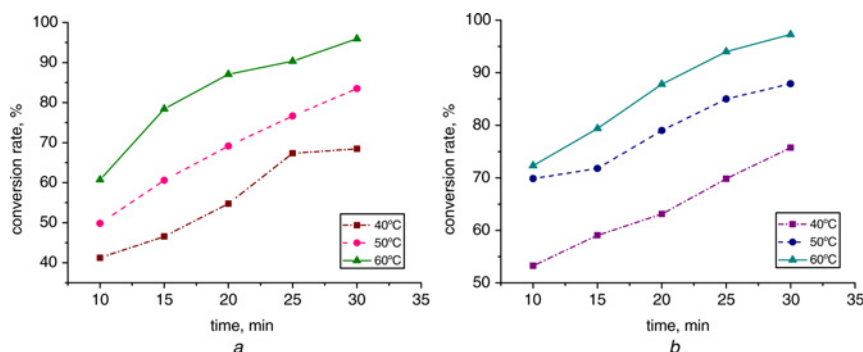

Figure 5 *Conversion rates*
a $Na_5P_3O_{10}$ against irradiation time at different reaction temperatures
b $C_3H_7Na_2O_6P$ against irradiation time at different reaction temperatures

an absolute temperature T, the fraction of molecules that have a kinetic energy greater than E_a could be calculated from statistical mechanics and Maxwell-Boltzmann distribution. The function of the Maxwell-Boltzmann distribution a directly proportional to absolute temperature T.

3.3. Kinetic study: the pseudo-first-order equation: The UV photocatalysis oxidation of organic matter follows the psuedo-first-order equation [8, 12], shown as the following:

$$\ln(c_t/c_0) = -kt \qquad (7)$$

where k is the pseudo-first-order rate constant, t is the reaction time and c_t and c_0 are the compound concentration at the irradiation time t and the initial concentration, respectively. The slope of the plot of $\ln(c_t/c_0)$ against time gives the value of rate constant k ($\min^{-1}$). The rate constant k could directly show the oxidation capability of UV photocatalysis at different conditions.

The values of k at different concentrations of H_2O_2 and different temperatures were obtained according to the pseudo-first-order equation, as shown in Table 1. Figs. 6a and b respectively, show the plots of k against H_2O_2 concentrations and temperature.

Table 1 Values of k at different concentrations of H_2O_2 (a) and different temperatures (b)

	Compounds	k, $\min^{-1}$	R^2
Concentration of H_2O_2, mg/l (a)			
247	$Na_3P_3O_{10}$	0.0144	0.9447
	$C_3H_7Na_2O_6P$	0.019	0.9853
493	$Na_3P_3O_{10}$	0.0235	0.9643
	$C_3H_7Na_2O_6P$	0.0238	0.9976
740	$Na_3P_3O_{10}$	0.0339	0.9221
	$C_3H_7Na_2O_6P$	0.0306	0.9787
987	$Na_3P_3O_{10}$	0.0257	0.9209
	$C_3H_7Na_2O_6P$	0.0223	0.9766
Temperature, °C (b)			
25	$Na_3P_3O_{10}$	0.0131	0.9215
	$C_3H_7Na_2O_6P$	0.0200	0.9902
40	$Na_3P_3O_{10}$	0.0347	0.9268
	$C_3H_7Na_2O_6P$	0.0323	0.9699
50	$Na_3P_3O_{10}$	0.0568	0.9491
	$C_3H_7Na_2O_6P$	0.0492	0.9562
60	$Na_3P_3O_{10}$	0.1068	0.9710
	$C_3H_7Na_2O_6P$	0.0972	0.9788
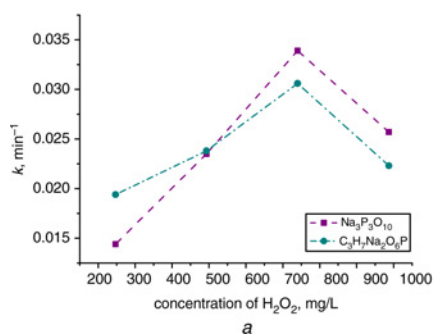
As shown in Fig. 6a, the rate constant k increased with the increase of the concentration of H_2O_2 when the concentration of H_2O_2 was lower than 740 mg/l. When the concentration of H_2O_2 is higher than 740 mg/l, the value of k decreased with increase of the concentration of H_2O_2. The plots of k against temperature for two typical TP components during the thermal-assisted UV digestion process are shown in Fig. 6b. With the increase of the reaction temperature, the values of k increased, but did not become linear. The increase of the rate constant became sharper at a higher temperature. For both these two digestion processes, the variation trends of rate constant k performed with the same characteristics as that of the conversion rates.

At the experimental condition of this Letter, the rate constants of $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ for the individual UV digestion processes were 0.0131 and 0.0200 $\min^{-1}$, respectively. For the H_2O_2-assisted UV digestion process, the optimum rate constants of $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ were 0.0339 and 0.0306 $\min^{-1}$, respectively. The optimum rate constants of $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ for the thermal-assisted UV digestion process were 0.1068 and 0.0972 $\min^{-1}$, respectively. As these results show, both H_2O_2 and heating could improve the efficiency of the UV photocatalytic digestion process. However, by comparison, the enhancement of heating on the UV photocatalysis process is more distinct than H_2O_2. In addition, the thermal-assisted UV digestion process will not lead to secondary pollution since no oxidant is needed in this digestion process, which makes it more compatible with the electrochemical detection of TP.

3.4. Analytical performance in real water samples: Since the thermal-assisted UV digestion process had a higher efficiency, this method was employed to digest real water samples collected from lakes and rivers around Beijing. The experimental results were compared with that using the standard autoclave persulphate oxidation method. The digestion condition of the thermal-assisted UV digestion process was 60°C and 30 min. The measurement results are shown in Table 2. It is found that the conversion using the thermal-assisted UV digestion method is consistent with that using the standard autoclave persulphate oxidation method.

Table 2 TP analysis with the thermal-assisted UV digestion process in real water samples

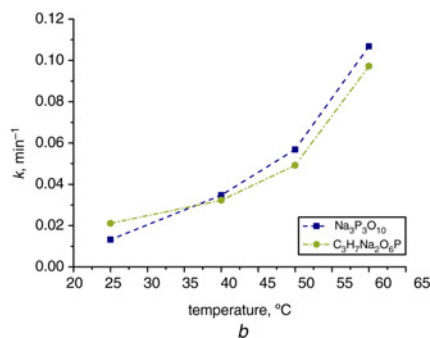| Water samples	Digestion method		Conversion rate, %
	Thermal-assisted digestion method, mg/L	Traditional method, mg/L	
1	0.2834	0.3076	92.13
2	0.1593	0.1660	96.00
3	0.1460	0.1504	88.56

Figure 6 *Values of k against H_2O_2 and against digestion temperature*
a k against H_2O_2 concentration
b k against digestion temperature

4. Conclusions: In this Letter, the thermal-assisted UV and H_2O_2-assisted UV oxidation methods utilising nanoTiO$_2$ photocatalyst are presented for the digestion of TP in water. The photocatalytic experiments for TP digestion were conducted using a 365 nm wavelength UV light, and TiO$_2$ nanoparticles immobilised on a silicon wafer as the photocatalyst. $Na_5P_3O_{10}$ and $C_3H_7Na_2O_6P$ were used as the typical components of TP. The effects of reaction time, H_2O_2 concentration and temperature were studied for the digestion of TP. For the H_2O_2-assisted UV digestion process there is an optimum concentration to obtain the maximum digestion efficiency and the optimum concentration of H_2O_2 obtained in this work is 740 mg/l. For the thermal-assisted UV digestion process, the digestion efficiency increases with the increase of reaction temperature.

The rate constants k of two phosphorus compounds for the UV digestion processes were obtained according to the pseudo-first-order equation. Both H_2O_2 and heating can improve the efficiency of the UV photocatalysis oxidation method. By comparison, the enhancement of heating on the UV photocatalysis process is more distinct than H_2O_2. In addition, the thermal-assisted UV digestion process will not lead to secondary pollution since no oxidant is needed in this digestion process, which makes it more compatible with the electrochemical detection of TP. Owing to the higher efficiency, the thermal-assisted UV digestion method was used in the digestion of real water samples. Compared with the conventional thermal digestion method for TP detection, this thermal-assisted UV digestion method decreases the digestion temperature from 120 to 60°C within the same time, which enables the digestion process to work at normal pressure.

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