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# $Bi_{25}FeO_{40}$ microspheres loading on g-$C_3N_4$ for high efficiency pollutants photodegradation

Xuan Sang Nguyen

Environmental Engineering Institute, Viet Nam Maritime University, Vietnam

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***Abstract*— $Bi_{25}FeO_{40}$/g-$C_3N_4$ composites were synthesized for dechlorination of 2-chlorophenol (2-CP). The characteristic of the obtained products was studied using the X-ray diffraction (XRD), (FESEM) scanning electron microscopy, UV-vis reflectance. The effects of g-$C_3N_4$ content, photocatalyst dosage, solution pH, $H_2O_2$ on the dechlorination efficiency were investigated, in addition to the reusability of the nanocomposites. The results showed that increasing content of $Bi_{25}FeO_{40}$ in nanocomposites, from 10 to 30 wt.%, greatly increased the dechlorination efficiency. $Bi_{25}FeO_{40}$/g-$C_3N_4$ 20wt.% and initial pH below 6.0 was the optimal conditions for the catalytic dechlorination of 2-CP. About 94.5% of 2-CP were completely removed after 150 minutes reaction at initial pH value of 6.0. The composites were easily separated from the solution by an applied magnetic field. The removal efficiency of 2-CP slightly decreased to 90% when the catalyst was reused in 4 runs. Therefore, $Bi_{25}FeO_{40}$/g-$C_3N_4$ composites can be considered as a promising method for remediation of pollution by 2-CP.***

***Keyword*— $Bi_{25}FeO_{40}$; photo-Fenton; Cluster microspheres.**

## I. INTRODUCTION

Recently, great attention has been paid for the morphology control of nanometer- and micrometer-size catalyst materials because of their interesting physical and chemical properties. Then, these materials can using widely in practice fields [1-3]. In this respect, a great number of remarkable approaches have been studied to controlling-synthesis the morphologies and facets exposed, wether in nanoscale or microscope [4, 5].

Recently, 2-chlorophenol is widely used in daily chemical and pharmaceutical industries. It is also a significatn intermediate of some medicines. Therefore, 2-CP causes the serious pollution in industrial wastewater. Some catalysts prepared from precious metals and their alloys have been applicated to remove 2-CP. However, noble metals are expensive cost. To solve this problem, catalysts based on metals and their alloys as Fe, Cu and Bi were developed due to their earth-abundant, low-cost and less toxic. For example, the magnetically recyclable Bi/$Bi_{25}FeO_{40}$-C nanocomposites were prepared via a one step hydrothermal method and exhibited high photocatalytic activity in hydrogen generation. Magnetic $Bi_{25}FeO_{40}$-graphene photocatalysts were fabricated by alkaline hydrothermal approach and showed enhanced catalytic activity for the removal of methylene blue (MB) under visible-light irradiation [6].

Due to the interesting characteristic, g-$C_3N_4$ is considered to be the most stable allotrope among various carbon nitrides under ambient conditions. Because of the two-dimensional frameworks of tri-s-triazine connected via tertiary amines structure , g-$C_3N_4$ possess high stable thermal and chemical stability. G-$C_3N_4$ is founded to be a visible-light-active polymeric semiconductor with a band gap of ~2.7 eV, corresponding to an optical wavelength of ~460 nm. Specially, it have an appropriate band structure for both water reduction and oxidation. As such, g-$C_3N_4$ is considered become the shining star in the field of photocatalysis.

In this work, $Bi_{25}FeO_{40}$/g-$C_3N_4$ composites were synthesised through a simple hydrogenthermal method. The catalyst activity of $Bi_{25}FeO_{40}$ photocatalysts were investigated by the photo-degradation 2-CP under visible light. The factors influential to the efficiency of the photo-dechlorination process are also studied and discussed in detail as the effects of $g\text{-}C_3N_4$ content, photocatalyst dosage, solution pH. The result show that $Bi_{25}FeO_{40}/g\text{-}C_3N_4$ composites can be considered as a promising approach for 2-CP removal.

## II. EXPERIMENTAL

### 2.1 Synthesis of composites.

Pure $g\text{-}C_3N_4$ powder was prepared using melamine as a precursor at 550 $^0$C for 4h in a muffle furnace. The obtained products were washed several times with de-ionized water then grounded for further use. Microsphere $Bi_{25}FeO_{40}$ was synthesized via a normal hydrothermal process. In a typical procedure, a certain amount of $Fe(NO_3)_3{\cdot}9H_2O$ (2,04 g ) and $Bi(NO_3)_3{\cdot}5H_2O$ (2,62 g) were dissolved in 60ml of deionized water under magnetic stirring. The precipitate was put into a Teflon-lined autoclave, followed by adding with 10 mL of sodium alginate solution (10 g/L), 4.5g of citric acid and a certain amount of KOH. After 30 min ultrasonic treatment, the mixture was transfered into a Teflon liner of 100mL capability. The autoclave was sealed and heated at 180°Cfor 12h and cooled to room temperature naturally. The resulting precipitant was recovered by filtration, followed by washing with distilled water three times, and drying at 80°C for 10h.

The $Bi/g\text{-}C_3N_4$ composite was prepared by simple impregnation method. A mount of 0.5 g $Bi_{25}FeO_{40}$ was added into 50 ml of ethanol under ultrasonic treatment for 40 min. Then, a certain amount of $g\text{-}C_3N_4$ added into the $Bi_{25}FeO_{40}$ suspension under vigorously stirring for 5 hours. The mixture was separated from the solution by an internal magnet, then washed and dried at 100$^0$C for 12h in an electric oven. The as-prepared composites were named x% $Bi/g\text{-}C_3N_4$ (x% denotes t mass percentages of $g\text{-}C_3N_4$ in as obtained-composites). In this work, $Bi/g\text{-}C_3N_4$ composite with 10 wt%, 20 wt% and 30 wt% of $g\text{-}C_3N_4$ were synthesized, respectively.

### 2.2 Characterization

X-ray diffraction (XRD analysis was carried out an X-ray powder diffractometer with Cu Kα radiation at 40 kV and 40 mA. The morphology and internal structure of the prepared samples were further checked by transmission electron microscopy (FESEM), using a JEM 2100F electron microscope operated at a voltage of 200 kV. UV–vis reflectance spectra of the powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using an RSAPE-20 reflectance spectroscopy accessory (Labsphere Inc., NorthSutton, NH). The PL spectra of products were measured by a transient fluorescence spectrometer (Shimadzu RF-5301PC).

### 2.3 The photo-degradation of 2-CP

The degradation experiments were carried out under single wavelength light (PL-LED 100F λ=410 nm). 2-CP were used as the model pollutant to evaluate the Fenton activity of the $Bi/gC_3N_4$ composites. In a typical process, 10 mg of $Bi/gC_3N_4$ composite was added into 100mL of the 2-CP (10mg/L) aqueous solution with countinuous stirring. Before illumination, the suspension was stiring in dark for 30 minutes to reach adsorption-desorption equilibrium. Then 0.1ml of the $H_2O_2$ aqueous solution (30%) was added to the reaction solution at the beginning of the illumination. About 5ml of the suspension were collected after a defined time and centrifuged to remove the photocatalyst for UV-vis spectrum measurement.

## III. RESULT AND DISCUSSION

### 3.1 XRD analysis

Fig.1 shows X-ray diffaction pattens of $g\text{-}C_3N_4$, $Bi_{25}FeO_{40}$ and $Bi/gC_3N_4$ 20% wt. The patterns showed the sharp and intense peaks indicating the photocatalysts were well crystallized. As shown in the Fig. 1, the XRD peaks of the $Bi_{25}FeO_{40}$ were observed agree with the sillenite-type structure (JCPDS 46-0416). The strong and sharp diffraction peaks signify exbihite the high crystallinity of $Bi_{25}FeO_{40}$. The two characteristic peaks of $g\text{-}C_3N_4$ at 13.28 and 27.33 can be indexed to (100) and (002) diffraction planes (JCPDS 87-1526) [7, 8]. Compared to pure $g\text{-}C_3N_4$, it can be seen clearly most peaks for $Bi_{25}FeO_{40}/g\text{-}C_3N_4$ indexing to the structure of $Bi_{25}FeO_{40}$. Because of the presence of $Bi_{25}FeO_{40}$, the peaks of $g\text{-}C_3N_4$ became weaker. The character of $g\text{-}C_3N_4$ could not be obtained in the XRD pattern of 20% $Bi/g\text{-}C_3N_4$ composite sample could be explained by the low adding content and well dispersion of $g\text{-}C_3N_4$ powders. However, g-C3N4 can still be found in the composites due of the appearance of the peak at 27$^0$. The results suggests the composites were formed between $g\text{-}C_3N_4$ and $Bi_{25}FeO_{40}$.

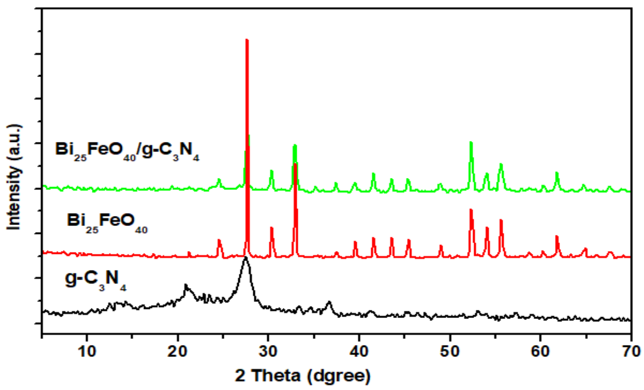


*Fig. 1. XRD pattern of $g\text{-}C_3N_4$, $Bi_{25}FeO_{40}$ and $Bi_{25}FeO_{40}/gC_3N_4$ 20% wt*

### 3.2 SEM analysis

The surface properties of $Bi_{25}FeO_{40}$ and $Bi_{25}FeO_{40}$/g-$C_3N_4$ composite photocatalyst was observed using SEM method. The obtained results are depicted in Fig. 2. As shown in Fig. 2A, the material is composed of a large quantity of well-dispersed microspherical particles. These particles have uniform size and shape, most of which are spheres of 300-500 nm. From Fig. 2B, it is seen that the surface of the samples became rough when the g-C3N4 was modified with $Bi_{25}FeO_{40}$. The surface of $Bi_{25}FeO_{40}$ was cover by g-C3N4 particles. After loading with g-$C_3N_4$, accommodation of g-C3N4 on the surface of $Bi_{25}FeO_{40}$ lead to the formation of a tight heterostructure. In this case, two phases of g-$C_3N_4$ and $Bi_{25}FeO_{40}$ are clearly seen and close contact to form an intimate interface. This is similar to previous reports [9-11]. It is found that cavitations created in sonochemical technique play an important role in the preparation of heterostructure materials. This can promote the formation of the stable hybrid structure between g-$C_3N_4$ and $Bi_{25}FeO_{40}$ composite [12].

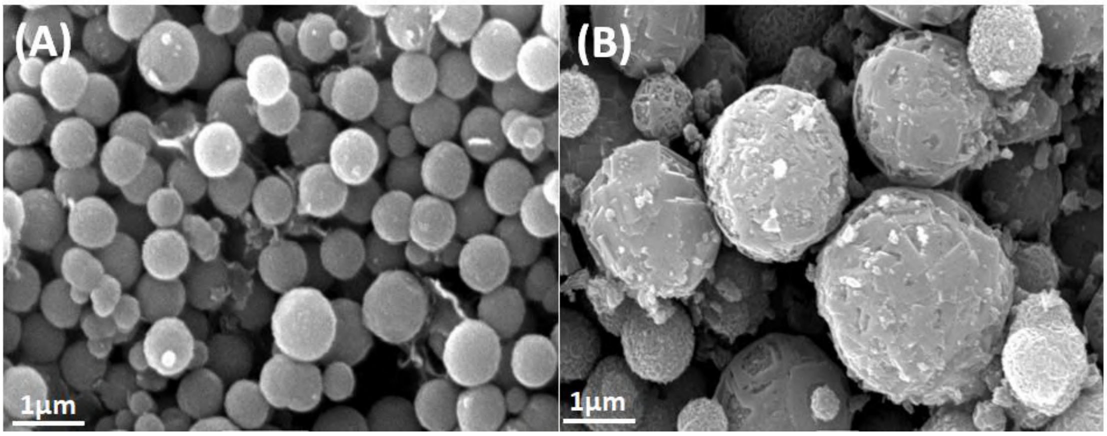


*Fig. 2. SEM image of the as-prepared $Bi_{25}FeO_{40}$ microspheres and $Bi_{25}FeO_{40}$/g-$C_3N_4$ microspheres*

**3.4 Photo-degradation of 2-CP**

The photocatalytic reaction of the $Bi_{25}FeO_{40}$/g-$C_3N_4$ catalysts were evaluated through the degradation of 2-chlorophenol (2-CP) in the presence of $H_2O_2$ with visible-light. The results of photocatalytic activities of the samples prepared at different conditions are shown in Fig. 3. When the photocatalyst is absence, no photodegradation can be observed. The photocatalytic activity of the Bi/g-$C_3N_4$ composite with visible light are further investigated by comparison with that of pure two-component. The Bi/g-$C_3N_4$ composite are much more photocatalytically efficient than pure $Bi_{25}FeO_{40}$ and pure g-$C_3N_4$. As shown in Fig.3a, about 94.5 % of 2-CP is photodegraded for 150 minutes of visible light irradiation while only 31% and 42% of 2-CP reduced with pure g-$C_3N_4$ and $Bi_{25}FeO_{40}$ microspheres used**,** respectively.

To understand the effect of g-$C_3N_4$ amount on $Bi_{25}FeO_{40}$/g-$C_3N_4$ composite, Bi/g-$C_3N_4$ 10%, 20% and 30% wt composites were used for the photodegradation of 2-CP. From Fig. 3b, it can be observed that 94%, 87%, and 66% 2-CP was degraded in the present of g-CN/ZnFe 20%, 10% and 30%, respectively under the same time irradiation. It can be learned from the results that amount g-$C_3N_4$ introduced into the $Bi_{25}FeO_{40}$ is one of pivotal role for photocatalytic efficiency. When introduced g-$C_3N_4$ amount in the composites is over 30%, the photocatalytic activity is reduced. This can be explained that with suitable content g-$C_3N_4$ added, the interfacial interaction can be formed between g-$C_3N_4$ and $Bi_{25}FeO_{40}$ which resulting on the improved transfer and separation of photogenerated electron/hole pairs [13]. Whereas, increasing further content of g-$C_3N_4$ in the composite would form blocking on the reaction sites of $Bi_{25}FeO_{40}$ , which can make their active sites reduced [14].

The excellent photocatalytic performance of $Bi_{25}FeO_{40}$/g-$C_3N_4$ composite can be attributed to their high crystalline and hibrid structure. The tight binding of g-$C_3N_4$ and $Bi_{25}FeO_{40}$ is suitable for the charge transfer between these two semiconductors and leads to a high separation rate of photogenerated electron-hole pairs while comparing to a physical mixture of two-component. As a result, these composites with a hybrid structure would result in an electric field at the interface, then improving the photocatalytic activity. The mineralization of 2-CP was also investigated as depicted in Figure 3c. The results reveal that the TOC removal of 2-CP using $Bi_{25}FeO_{40}$/g-$C_3N_4$ composites as catalysts achieved about 74 %. The results suggest that as-synthesized cluster microspheres show high capacity for the mineralization of 2-CP pollutants.

Effect of catalyst amount and pH in the range of 2 to 8 on 2-CP photo-degradation efficiency was also valued as depicted in Fig. 4. The results show that the degradation rate of 2-CP improved with an increase in catalyst amount, as shown in Fig. 4a. However in higher catalyst dosage, the 2-CP removal percentage slightly decreased. Based on the experiment, 10 mg/L of the as-prepared composite is optimum dose for the 2-CP photo-dechlorination. The experiment results on the effect of pH reveal that the optimum pH was 6.0 (see at Fig. 4b). With pH below 6.0, in high $H^+$ concentration, the formation of stable oxonium ion $[H_3O_2]^+$ makes hydrogen peroxide more stable and then decreases its activity with ferrous ions. Moreover, the formation of Fe(II) complexes and ferric oxyhydroxides precipitation at a pH above 5.8 are probably reasons for efficiency decreases in the 2-CP removal processes.

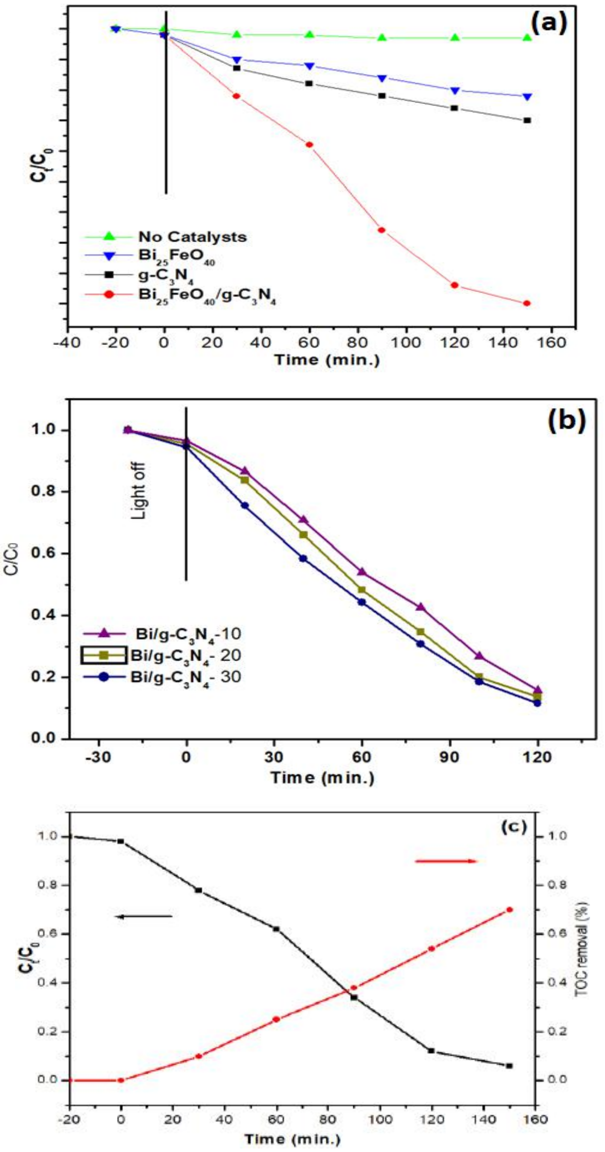


*Fig. 3. (a) The 2-CP photo-degradation with different photocatalysts under visible light; (b) The 2-CP photo-degradation with Bi/gC3N4 composites of 10,20,30 wt%. (c) The mineralization of 2-CP using $Bi_{25}FeO_{40}$/g-$C_3N_4$ composite under visible light.*

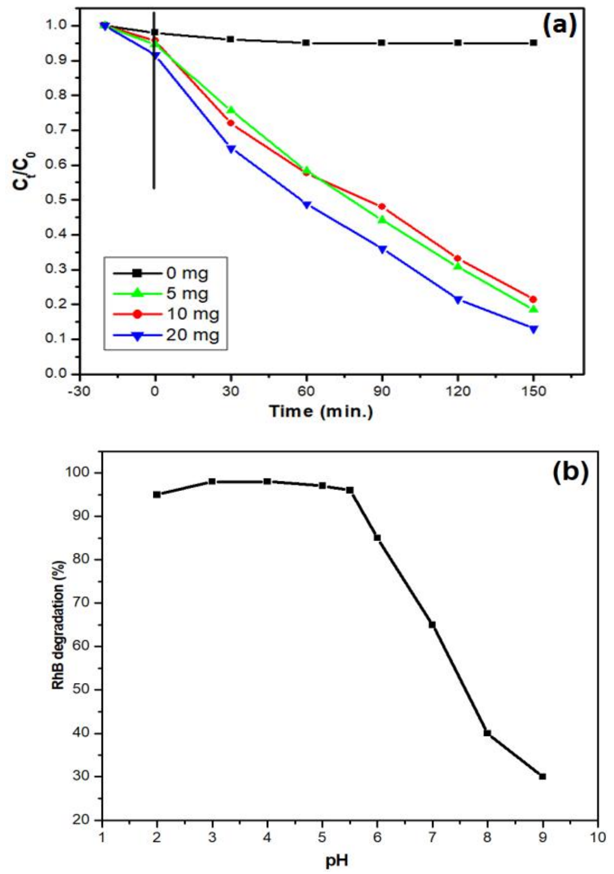


*Fig. 4. The effect of (a) catalyst amount and (b) pH on 2-CP removal %*

As known, the Fenton reaction is one of the most effective advanced oxidation processes for wastewater treatment in which the active hydroxyl radicals generated by reaction between $Fe^{2+}$ and $H_2O_2$. It is reported that the presence of $Fe^{2+}$ in the oxide plays an important role for the activation of $H_2O_2$[15, 16]. With the present of both visible light and $H_2O_2$, active hydroxyl radicals will be generated by main reactions following:

$$H_2O_2 + Fe\ (II) \rightarrow Fe\ (III) + {}^{\bullet}OH + OH^- \quad (3)$$

$$Fe\ (III) + e^- \rightarrow Fe\ (II) \quad (4)$$

Then more •OH can be produced resulting in a reaction between regenerated Fe(II) with $H_2O_2$ (Eq. (1)). Therefore, the kinetics of the reaction between $^{\bullet}OH$ and 2-CP is improved remarkably via visible light irradiation[16]. Moreover, the improvement of the photo-Fenton reaction of the as-prepared composite could be ascribed to the electron transfer process accelerated. As a result, the interface between $Fe^{3+}$ and $H_2O_2$ improved, which result in more ·OH radical from high rate of decomposition $H_2O_2$ [17]. Furthermore, the crystalline structure and hybrid structure are important factors that could improve the photocatalytic perform of the as-obtained Bi/g-$C_3N_4$.

To investigate the stability of the Bi/g-$C_3N_4$ composites, the recycle tests were conducted in the oxidation process under Vis light irradiation. The results reveal that the as-obtained composite was easily collected by an internal magnet and the 2-CP degradation effectively has no significant change during the 4th successive cycles, demonstrating the high stability of the composite (Fig. 5). The chracteristic plays a very important role in application for water treatment at industry scale. The high photocatalytic activity, the stability and the easily separation suggest that the Bi/g-$C_3N_4$ can be promising candidates for the 2-CP dechloronation application.

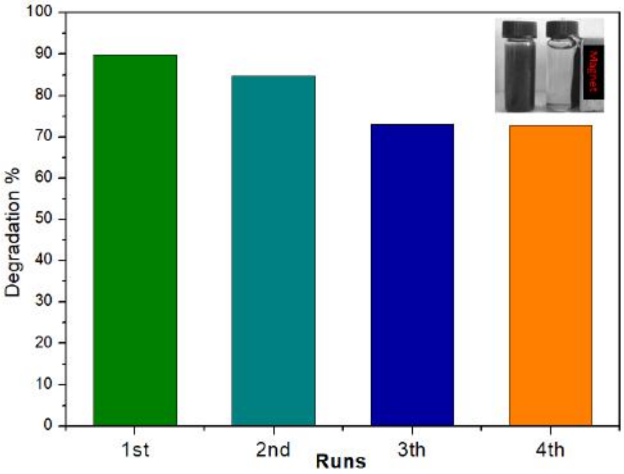


*Fig. 5. The stability of the Bi/g-$C_3N_4$ composites after 4 recycles*

## IV. CONCLUSION

A series of magnetic separable $Bi_{25}FeO_{40}$/g-C3N4 composite was successfully prepared by simple solvothermal method. The optimized weight ratio of g-$C_3N_4$ and $Bi_{25}FeO_{40}$ was observed. The results showed that $Bi_{25}FeO_{40}$/g-CN composite with added 20% g-$C_3N_4$ exposed the highest activity for 2-CP dechlorination under visible light irradiation. The improved photocatalytic activity of 20% Bi/g-CN can be attributed to their high crystalline and hibrid structure. The tight binding of g-$C_3N_4$ and $Bi_{25}FeO_{40}$ is suitable for the charge transfer between these two semiconductors and leads to a high separation rate of photogenerated electron-hole pairs while comparing to a physical mixture of two-component. As a result, these composites with a hybrid structure would result in an electric field at the interface, then improving the photocatalytic activity. Specially, Bi/g-$C_3N_4$ can be collected easily by using an external magnetic field and exhibit the high stability after 4 runs. These properties of the Bi/g-$C_3N_4$ composites as prepare could be a promising photokklcatalyst for the degradation pharmaceutical contaminants.

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