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Research on TiO_2-Based Photocatalyst Thin Film and Its Application in a Pilot-Scale Supply Water Treatment System

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Abstract

In order to utilize the abundant natural sunlight in Hochiminh City for energy-saving purpose, the application of TiO_2-based photocatalyst thin film coated on ceramic beads in a pilot-scale supply water treatment system of 2 m^3/day was studied in this present work. The photocatalyst thin film was prepared by sol-gel and spray coating methods. The derived photocatalyst thin film presented high BET specific surface area of more than 160 m^2/g while it also maintained good crystallinity. These superior physicochemical properties of the photocatalyst were well consistent with its strong photoactivity in the pilot-scale supply water treatment system. Groundwater after passed through ferric removal and sand-filter systems was treated in the pilot-scale supply water treatment system using the photocatalyst thin film. The COD, TOC and coliform removal efficiencies were measured at 63%, 51% and 100%, respectively by using the above system under natural sunlight in Hochiminh City.

Keywords*:* photocatalysis; TiO_2 thin film; supply water treatment; pilot-scale

1. Introduction

As the life styles and living environment change rapidly, the growth in environmental catalyst technology has been observed to meet the demand of human beings for the control of residential environments, e.g., antimicrobial activity and odor control (Yogo and Ishikawa, 2000). The higher the demand for the control of residential environments, the stronger the demand of human for energy. Nevertheless, the energy for our daily life currently depends essentially on fossil fuel that is the main source of greenhouse effect and predicted to become shortage in the coming decades (Yogo and Ishikawa, 2000). As a consequence, sustainable development has been much paid attention by many scientists to keep our planet green. Among the sustainable technologies, solar environmental treatment has been intensively and extensively studied in recent years (Lonnen *et al.*, 2005). One of the popular applications of this technology is solar disinfection of drinking water contaminated with bacterial (Smith *et al.*, 2000) and viral (Sommer *et al.*, 1997) pathogens, especially in those developing countries where safe and reliable drinking water is not available all year round (Conroy *et al.*, 2001).

In this present study, in order to utilize the abundant natural sunlight in Hochiminh City for energy-saving purpose, the application of gel-derived TiO_2-SiO_2 photocatalyst thin film coated on ceramic beads in a pilot-scale supply water treatment system of 2 m^3/day was studied. The photocatalytic activity of catalyst thin film was tested in terms of chemical oxidation demand (COD), total organic carbon (TOC) and coliform removal under both UVA light and natural sunlight irradiation. Because *E. coli* is a common type of bacteria that can cause foodborne and waterborne illness, it was employed as a target microorganism for the photocatalytic removal in this present work.

2. Materials and Methods

The procedures of preparation of TiO_2-SiO_2 sol-gel solution were mentioned in details in our previous study (Nguyen and Nguyen, 2007). Three solutions were first prepared: the first solution denoted as S1 was prepared by mixing solvents (a mixture of ethanol and iso-propanol with the volume ratio = 1:1) with water and nitric acid; the second one included the solvents, water and tetraethyl orthorsilicate (TEOS, Merck), which was strongly mixed in a beaker at ca. 300 rpm; the third solution was a mixture of the solvents and titanium (IV) isopropoxide (TTIP, Merck). The above three solutions were then mixed and refluxed at 80 ^oC for 1 h under vigorous stirring (*ca*. 1500 rpm). The obtained sol-gel solution was thereafter hydrothermally treated in a lab-made autoclave at 150 ^oC for 10 h. TiO_2-SiO_2 thin film immobilized on support was thereafter prepared by spray coating method. The support employed in this present work was

Figure 1. Image of commercial ceramic beads with the average diameter of ca. 5 mm.

commercial ceramic bead with the average diameter of ca. 5 mm (Fig. 1) and the density in range of 0.8 – 1.2 kg/L. The ceramic beads were put into a spray chamber that was supplied with a flow of compressed air to maintain a fluidized bed for the beads. The TiO_2-SiO_2 sol-gel solution was simultaneously sprayed into the chamber for coating on the bead surface. After coating, the TiO_2-SiO_2 thin film coated beads were dried in an oven at 105 °C for 2 h and then calcined at 550 °C. In order to determine the thermal stability of catalyst, calcination of catalyst was also carried out at 900 °C for comparison. The floating and sinking beads were deliberately used in the photocatalytic reactor to maximize the exposure of catalyst to light irradiation as well as to the contaminants.

In TiO_2-SiO_2 mixed oxide, the TiO_2:SiO_2 weight ratio was controlled at 100:0, 90:10 and 95:5. The crystallinity of catalyst was measured by using X-ray diffraction (Rikagu, Cu K_α). For reasonable comparison of the crystallinity of different catalysts, the same procedures of measurement and amount of catalyst were maintained in all of the XRD measurements. The crystallinity of the catalyst is therefore estimated on the basis of the intensity of the anatase peak of the catalysts. The BET specific surface area of catalyst was determined by nitrogen adsorption at -196 °C (Chembet 3000). The bandgap energy of catalyst was estimated by using UV-Vis diffuse reflectance spectroscopy (Jasco 500).

Photocatalytic activity of the catalyst thin film was tested in a lab-scale batch reactor containing 250 mL of solution under UVA light (2 lamps with total capacity of 30W) and natural sunlight. The photoactivity of catalyst was also tested in a pilot-scale supply water treatment system under natural sunlight with the capacity of 2 m^3/day as shown in Fig. 2. Groundwater after passed through ferric removal and sand-filter systems is treated in the pilot-scale system. The system was operated with a continuous mode with water circulation using a submersible pump placed in a water container as shown in Fig. 2. The initial concentrations of *E. coli* in both reactors were in range of 10^4-10^5 cfu/mL. The density of *E. coli* in the reactor was determined by the pour plate method and calculated by the viable plate count method. 1 mL of suspension was withdrawn at each sampling and was diluted to 1/10, 1/100, 1/1000. Some of the samples were used as received without diluting. Finally 1 mL of the diluted or undiluted suspension was micropipetted into Petri plates to count the numbers of *E. coli* bacteria. Three replicate plates were used at each dilution. Then, warm agar was poured into plates. Petri plates were kept in an incubator at 37 °C in 12 – 18 h and the numbers of *E. coli* bacteria were counted in the next morning. An average count that used to determine the *E. coli* inactivation efficiency was calculated from the three plate counts. Because the numbers of *E. coli* bacteria in each reported result were determined on the basis of the average data of three experiments, the range of 10^4-10^5 cfu/mL of *E.*

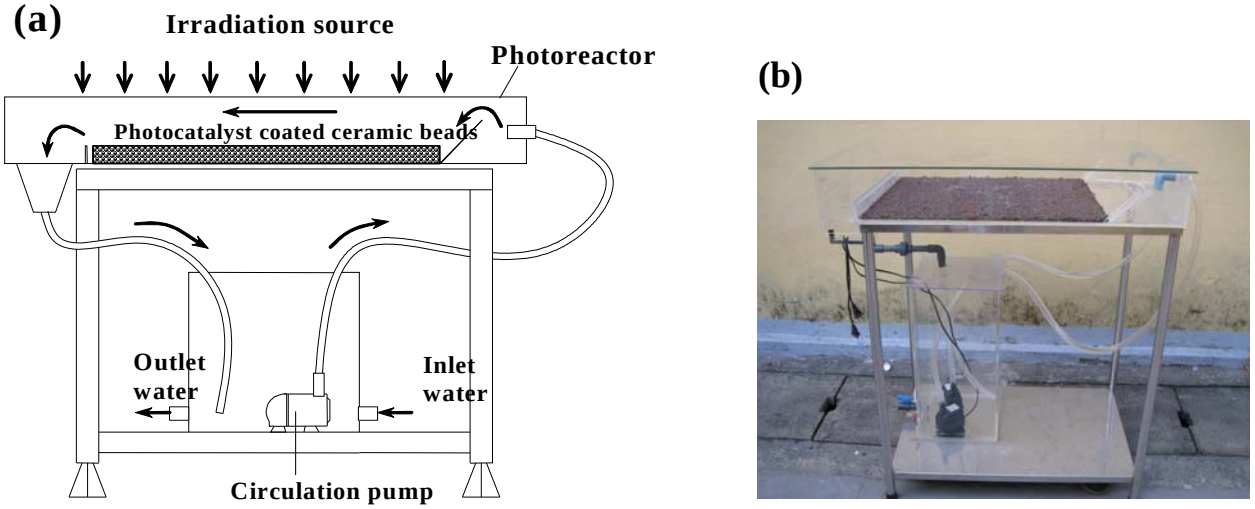

Figure 2. (a) schematic diagram and (b) real image of the pilot-scale supply water treatment system under natural sunlight with capacity of 2 m^3/day.

Table 1. BET specific surface areas of different catalysts

Catalyst	TiO_2:SiO_2 weight ratio	S_{BET} (m^2/g)
P25 (TiO_2)	100 : 0	53.11
TiO_2	100 : 0	82.74
TiO_2-SiO_2	95 : 5	143.50
TiO_2-SiO_2	90 : 10	164.54

coli could not substantially affect the inactivation efficiency results. The amounts of ceramic beads in the lab-scale and pilot-scale reactors were ca. 0.1 and 2.4 kg, respectively. The average amount of catalyst on 1 kg of ceramic beads was estimated at ca. 1 g. COD was measured with standard method. TOC and coliform were determined with a TOC analyzer (TOC-V_{CPH}, Shimadzu) and Most Probable Number (MPN) method, respectively. The sunlight intensity during the experiment time was estimated by using a lumen meter (Lux 5924, Hana).

3. Results and Discussion

3.1. Characterization of photocatalyst

Table 1 shows the BET specific surface area of different catalysts. Sol-gel method coupled with hydrothermal treatment is found to substantially improve the specific surface area of TiO_2 catalyst to more than 80 m^2/g as compared to only ca. 50 m^2/g of TiO_2-P25. The superior S_{BET} of the lab-made TiO_2 catalyst could be ascribed to the stable formation of crystals as well as micropores during the hydrothermal treatment process in the autoclave. In addition, as SiO_2 is added to TiO_2, it is observed to significantly increase the specific surface area of the derived TiO_2-SiO_2 catalyst as shown in Table 1. The BET specific surface area of TiO_2-SiO_2 (90:10) is around three times higher than that of bare TiO_2-P25.

Although SiO_2 is observed to enhance the specific surface area of derived TiO_2-SiO_2 catalyst, it still maintains the good crystallinity of the catalyst as depicted in Fig. 3. Furthermore, TiO_2-SiO_2 catalyst presents only anatase phase. This crystal phase is maintained up to the calcination temperature of 900 ^oC without any phase transformation from anatase to rutile [Fig 3(d)]. These results imply that TiO_2-SiO_2 catalyst synthesized in this present work is very stable in terms of crystallinity and high calcination temperature.

Fig. 4 presents the UV-Vis spectroscopies of different catalysts. TiO_2-SiO_2 is found to slightly shift to UV range as compared to bare TiO_2, which is well consistent with the small decrease in the crystallinity of the TiO_2-SiO_2 catalyst as shown in Fig. 3. The blue-shift phenomenon of TiO_2-SiO_2 could result from the quantum-size effect that is caused by the decrease in the particle size of the catalyst (Nguyen *et al.*, 2006). The band-gap energies of the above catalysts are estimated in the range of 3.13 – 3.18 eV (with eV≈ 1239.95/λ, where λ is the wavelength in nm at the onset of absorption spectrum (Nguyen *et al.*, 2006)).

3.2. Photocatalytic removal of E. coli in the lab-scale reactor

Fig. 5 shows the *E. co*li removal efficiency of different catalysts in the lab-scale reactor under UVA light irradiation. TiO_2-SiO_2 (90:10) catalyst showed

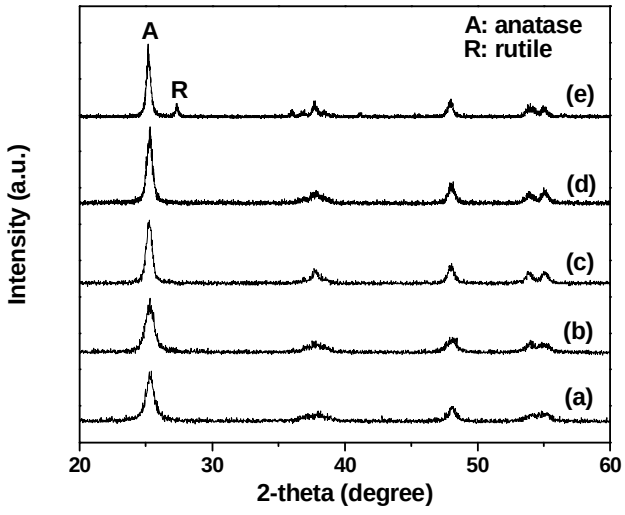

Figure 3. XRD patterns of different catalysts: (a) TiO_2-SiO_2 (95:5), (b) TiO_2-SiO_2 (90:10), (c) TiO_2-SiO_2 (100:0), (d) TiO_2-SiO_2 (95:5) calcined at 900 ^oC and (e) TiO_2-P25.

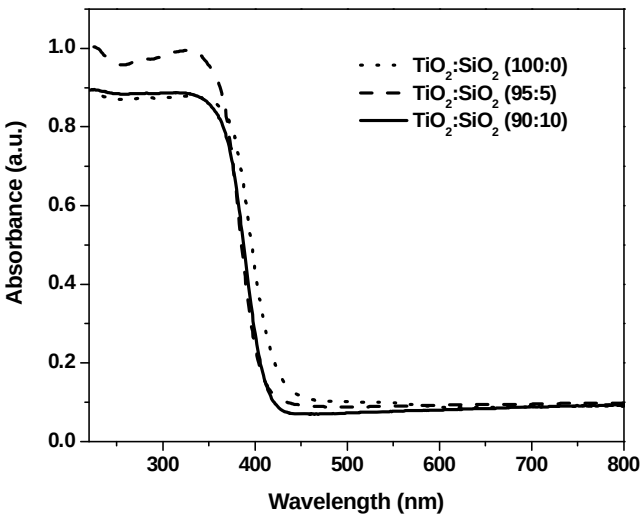

Figure 4. UV-Vis spectroscopies of different TiO_2-SiO_2 catalysts.

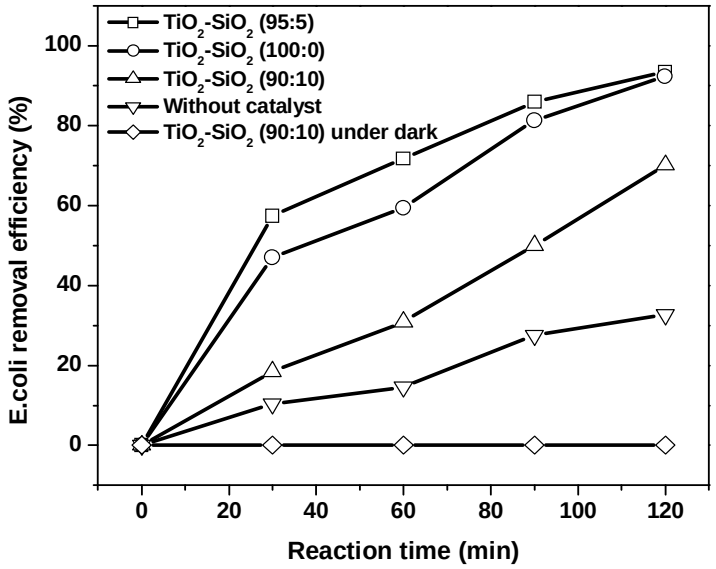

Figure 5. *E. coli* removal efficiency of different catalysts in the lab-scale reactor under UVA light irradiation.

negligible efficiency towards *E. coli* removal under dark. Accordingly, the reaction under dark was not tested in other experiments in this present work. UVA light alone is observed to decompose *E. coli* at ca. 30% after 2 h of irradiation. Meanwhile, UVA light irradiation in combination with TiO_2-SiO_2 (95:5) catalyst could remove up to ca. 94% *E. coli* after the reaction of 2 h. Nevertheless, TiO_2-SiO_2 (90:10) catalyst presents quite low efficiency towards *E. coli* removal with only around 70% after 2 h of irradiation. This result could be ascribed to the low crystallinity of TiO_2-SiO_2 (90:10) catalyst. Although the S_{BET} of bare TiO_2 catalyst is two times lower than that of TiO_2-SiO_2 (90:10) counterpart, the *E. coli* removal efficiency of the former is much better than that of the latter. TiO_2-based catalyst with high specific surface area generally results from its small particle size (20-50 nm) which may penetrate into bacteria (~1 μm) to cause intercellular damage (Srinivasan and Somasundaram, 2003). Nevertheless, the small particles in the catalyst could easily form aggregates under some circumstances. Accordingly, bacteria removal efficiency may not be solely affected by the specific surface area of the catalyst. Meanwhile, good crystallinity of a catalyst is inherently based on the regularity of the catalyst lattice, which significantly improves the production of free electrons and holes in the lattice for a photocatalytic reaction (Nguyen and Yang, 2003). In other words, the results in Fig. 5 imply that not only the specific surface area but also the crystallinity of photocatalyst take essential roles in the disinfection function of the catalyst.

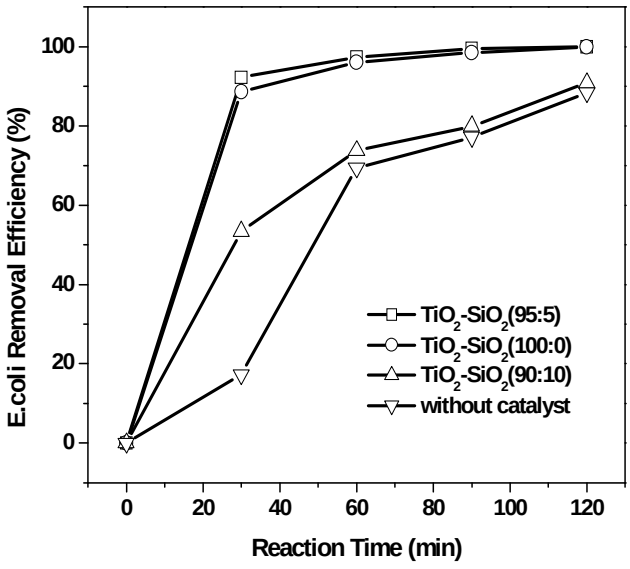

Figure 6. Photocatalytic removal of *E. coli* in the lab-scale reactor under natural sunlight irradiation.

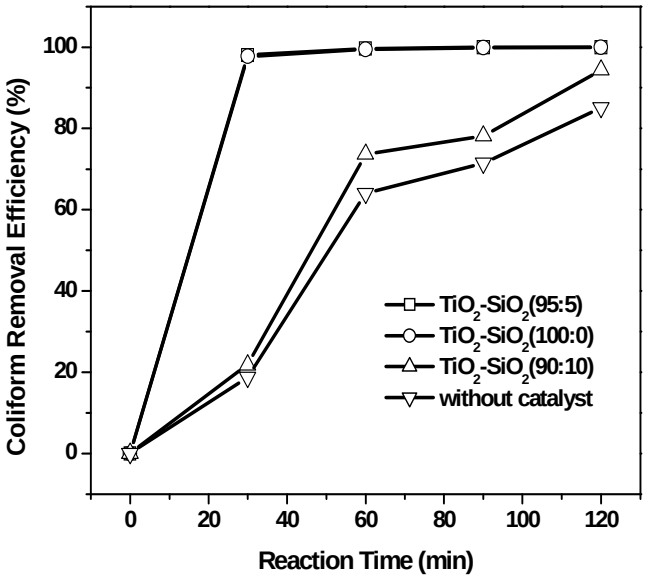

Figure 7. Photocatalytic removal of coliform in the pilot-scale reactor under natural sunlight irradiation.

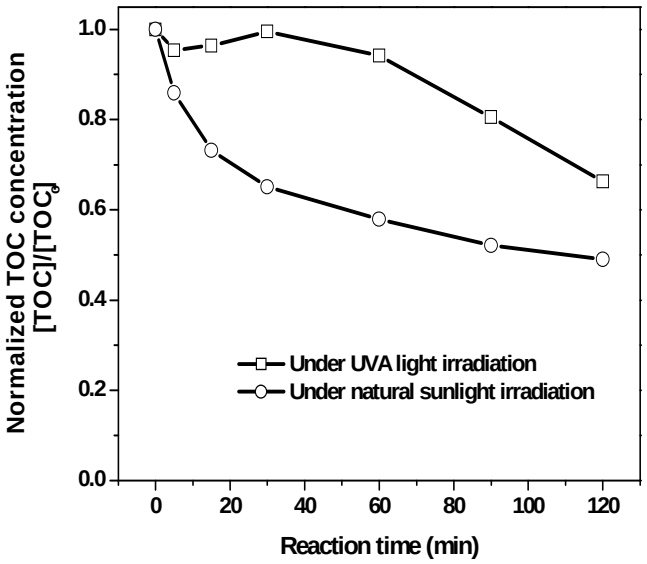

Figure 8. Time dependency of TOC concentration. The reaction was carried out by using TiO_2-SiO_2 (95:5) thin film in the pilot-scale reactor.

It is so interestingly found that the irradiation of natural sunlight in Hochiminh city is observed to significantly improve the photoactivity of TiO_2-based catalysts as shown in Fig. 6. Natural sunlight alone can remove up to 89% *E. coli* while it is observed to decompose 100% *E. coli* in the presence of either TiO_2-SiO_2 (95:5) or TiO_2-SiO_2 (95:5) catalyst after 2h of irradiation. The superior photoactivity of the catalysts could be ascribed to the strong intensity of natural sunlight in Hochiminh city. The average intensity of the natural sunlight is estimated at around 1 sun or 100 mW/cm^2. These results present the promising utilization of natural sunlight for the energy-saving environmental technologies.

3.3. Photocatalytic removal of coliform in the pilot-scale reactor

In order to test the feasibility of using TiO_2-SiO_2 thin film in a real disinfection system, the photocatalytic reaction towards coliform removal under natural sunlight is carried out in the pilot-scale reactor with the capacity of 2 m^3/day. The result of coliform removal efficiency in the pilot-scale reactor is found similar to that in the lab-scale counterpart as shown in Fig. 6 and Fig.7, respectively. The similarity of the results of two reactors strongly confirms the strong potential application of photocatalyst in a real supply water treatment system at the lowest cost.

3.4. Photocatalytic removal of COD and TOC in the pilot-scale reactor

Time dependency of the normalized TOC concentration is presented in Table 2. The result shows that organic compounds in the reaction solution are not easily decomposed into minerals at the initial time. There are only 18% of organic compounds that are mineralized after 90 min of irradiation. Meanwhile, as the reaction time is continued to further 30 min, about 34% TOC is observed to be decomposed. This phenomenon could be explained by the inactivation of bacteria during the initial reaction time. These bacteria are then decomposed into organic compounds that are finally mineralized on exposure to UVA light and photocatalyst after 2 h. The results of TOC removal are quite consistent with those of COD counterpart as shown in Table 2.

When the reaction is carried out under natural sunlight irradiation, the normalized TOC concentration

Table 2. COD and TOC of the reaction solution according to reaction time

Reaction time (min)	COD[a] (mg/l)	TOC[a] (mg/l)	COD[b] (mg/l)	TOC[b] (mg/l)
0	11.2	6.73	11.2	6.73
30	9.7	6.70	6.3	4.38
60	6.6	6.34	4.2	3.90
90	6.4	5.52	4.1	3.51
120	5.5	4.46	4.1	3.30

[a] The reaction was carried out by using TiO_2-SiO_2 (95:5) under UVA light irradiation.

[b] The reaction was carried out by using TiO_2-SiO_2 (95:5) under natural sunlight irradiation.

is interestingly found to rapidly decrease at the initial time as presented in Fig. 8. This result could be again ascribed to the strong intensity of natural sunlight in comparison with UVA light. The average intensity of the natural sunlight was estimated at around 1 sun or 100 mW/cm^2 that was much higher than the intensity of UVA light of around 15 mW/cm^2 in this present work.

4. Conclusions

Gel-derived TiO_2-SiO_2 photocatalyst thin film is immobilized on ceramic beads by spray coating method. The photocatalyst thin film presents the superior specific surface area of around 160 m^2/g while it also maintains good crystallinity. The photocatalyst thin film is employed in the pilot-scale supply water treatment system for COD, TOC and coliform removal. Under natural sunlight in Hochiminh city, the COD, TOC and coliform removal efficiencies are measured at 63%, 51% and 100%, respectively by using the above system with capacity of 2 m^3/day. The results present strong potential application of photocatalyst in energy-saving environmental treatment system.

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