

# Role of Na<sup>+</sup> ion removal on the photocatalytic properties of hydrothermally-prepared TiO<sub>2</sub> nanotubes

Naimat Abimbola Eleburuike, Wan Azelee Wan Abu Bakar<sup>\*</sup>, Rusmidah Ali

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

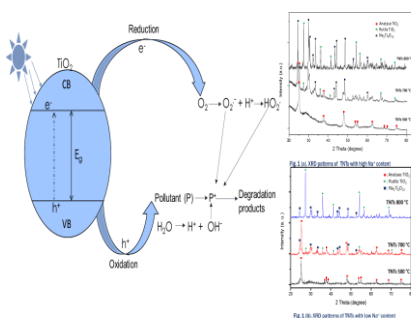
<sup>\*</sup> Corresponding author: wazelee@kimia.fs.utm.my

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## Graphical abstract



## Abstract

The hydrothermal preparation of TiO<sub>2</sub> nanotubes (TNTs) involves the use of highly concentrated NaOH solution which may result to having residual Na<sup>+</sup> ions in the TNTs, depending on the degree of acid washing. In this study, the role of Na<sup>+</sup> ions removal on the photocatalytic properties of hydrothermally-prepared TNTs was investigated. It was observed that the amount of residual Na<sup>+</sup> ions has significant effect on the crystal structure of TNTs. Hence, the effect of the residual Na<sup>+</sup> ions was studied at different annealing temperatures of 500, 700 and 800 °C. To understand the effect of the residual Na<sup>+</sup> ions on the photocatalytic activity of TNTs, the TNTs were applied to the degradation of aqueous solution of paraquat dichloride under UV light. It was observed that TNTs containing negligible amount of Na<sup>+</sup> ions demonstrated high photocatalytic activity at 500 °C annealing temperature while TNTs with high Na<sup>+</sup> ions content demonstrated highest activity at 800 °C. This is because TNTs with low Na<sup>+</sup> ions consisted of active crystalline anatase species at 500 °C. On the other hand, TNTs with high Na<sup>+</sup> ions content showed poor performance at 500 °C due to the presence of amorphous sodium titanate species which resulted in rapid electron-hole pair recombination. Generally, it can be concluded that TNTs containing negligible amount of Na<sup>+</sup> ions demonstrated excellent photocatalytic activity by achieving 77.1% degradation of paraquat dichloride compared to those containing high amount of Na<sup>+</sup> ions which achieved 61.1% degradation of paraquat dichloride in 5 h.

**Keywords:** Sodium ion, titanium dioxide, nanotubes, photocatalysis, paraquat dichloride

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## INTRODUCTION

TiO<sub>2</sub> has been recognized as a highly efficient photocatalyst for the degradation of organic pollutants due to its chemical and biological inertness, photo-corrosion stability, availability and cheap cost (Fujishima *et al.*, 2000). However, despite the effectiveness of this semiconductor nanoparticles, the fast recombination of the photogenerated electrons and holes pairs (e<sup>-</sup>/h<sup>+</sup>) during the photocatalytic process has led to low quantum yield and a reduction in the overall efficiency of the process (Singh *et al.*, 2013). Hence, research over the years has focused on methods to increase the life span of the charge carriers and one of the successful steps was modification of zero-dimensional (0D) TiO<sub>2</sub> nanoparticles (TNPs) to one-dimensional (1D) TiO<sub>2</sub> nanostructures in the form of nanorods, nanotubes and nanowires (Wang *et al.*, 2010). Reports showed that these 1D TiO<sub>2</sub> nanostructures have better electronic properties than TNPs due to better electrons mobility in these materials (Melcarne *et al.*, 2010; Li *et al.*, 2009). This has prevented the fast recombination of the e<sup>-</sup>/h<sup>+</sup> thus, leading to an increase in photocatalytic activity (Liu *et al.*, 2007). Furthermore, 1D TiO<sub>2</sub> are believed to possess excellent textural properties such as high surface area to volume ratio and high

porosity than their nanoparticles counterparts (Qamar *et al.*, 2008; Tsai and Teng, 2004). Photocatalytic testing of the 1D TiO<sub>2</sub> on the degradation of organic pollutants revealed that they demonstrated higher photocatalytic activities compared to TNPs (Jia *et al.*, 2009; Joo *et al.*, 2005). This study focused mainly on TiO<sub>2</sub> nanotubes (TNTs) prepared by hydrothermal method.

The hydrothermal formation mechanism of TNTs is generally based on exfoliation of TNPs in caustic alkaline NaOH solution into nanosheets of Ti-O-Na<sup>+</sup> which are subsequently rolled-up into titanate nanotubes during cooling or washing process with or without hydrochloric acid. The titanate nanotubes may have the formula H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>.nH<sub>2</sub>O, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>.nH<sub>2</sub>O, Na<sub>2</sub>HTi<sub>3</sub>O<sub>7</sub>.H<sub>2</sub>O, etc., depending on the degree of removal of Na<sup>+</sup> (Qamar *et al.*, 2008; Roy *et al.*, 2011). In another report, it was proposed that TNTs are formed by complete or partial dissolution of TNPs in concentrated NaOH solution, followed by nucleation and growth of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nano-intermediate, followed by splitting, wrapping and thickening into lamellar structures (Wu *et al.*, 2006).

The removal of Na<sup>+</sup> ions by replacing them with protons during the acid washing process is a vital step in the preparation of TNTs. The extent of Na<sup>+</sup> ions removal dictates the crystal structure of TNTs which in turn determines the photocatalytic activity. High Na<sup>+</sup> content

will lead to the presence of sodium titanate species in the TNTs which normally would reduce the quantity of active anatase and rutile TiO<sub>2</sub> present. Sodium titanate species are not photocatalytically active (Qamar *et al.*, 2008). Thus, TNTs with high amount of sodium titanate species are expected to exhibit poor performance compared to TNTs with predominantly anatase or rutile or both phases.

The annealing temperature plays a vital role in determining the crystallinity and phases of TNTs. Since the Na<sup>+</sup> ions content affects the crystal structure of TNTs, studying the photocatalytic properties of TNTs at different annealing temperatures is crucial. This will enable the determination of the best annealing temperature that will give the maximum photocatalytic efficiency for the TNTs with high or low Na<sup>+</sup> content. Three different annealing temperatures *viz.* 500, 700 and 800 °C were selected. The investigation of the effect of Na<sup>+</sup> ions content in TNTs as a function of the annealing temperature to achieve the best photocatalytic activities has not been explored yet in most of the earlier reports.

Hence, in this study, the effect of the extent of Na<sup>+</sup> ion removal was correlated with the annealing temperature to determine the most suitable crystal structure at which TNTs with high or negligible Na<sup>+</sup> content will be most active photocatalytically. To the best of our knowledge, there is no report on utilizing the annealing temperature to maximize the photocatalytic activity of TNTs with high Na<sup>+</sup> content. The findings of this study will be useful in terms of understanding the role that the extent of Na<sup>+</sup> ion removal plays in determining the crystallinity and photocatalytic activity of TiO<sub>2</sub> nanotubes and the effect of tailoring this activity through the annealing temperature.

The photocatalytic activities of the TNTs were measured based on the degradation of paraquat dichloride under UV light. Paraquat dichloride is a highly toxic, fast acting, non-selective contact herbicide. It has been detected in ground and surface water. Some documented health effects of paraquat exposure include endocrine disruption, Parkinson's disease, neurological disorder and cancer (PAN Germany, 2003; Neumeister and Isenring, 2011; Watts, 2012).

## EXPERIMENTAL

### Materials

The chemicals and reagents used for this study are all analytical grade and used without further purification. NaOH and HCl were obtained from QREc, paraquat dichloride and titanium tetrakispropoxide (TTIP) were obtained from Sigma-Aldrich, HNO<sub>3</sub> and ethanol were obtained from EMSURE.

### Preparation of TNTs

The preparation of TNTs was done according to the method previously reported (Eleburuike *et al.*, 2016). Briefly, TNPs were synthesized by sol-gel method as follows. 75 mL of TTIP was dissolved in 150 mL of ethanol. Then, another solution containing 100 mL ethanol and 13.5 mL of distilled water was gradually added to it under stirring. 0.5 mL HNO<sub>3</sub> was added as a catalysts during the hydrolysis of TTIP. The resultant milky sol was stirred for 1 h after which it was aged for 24 h. This was followed by drying in an oven for 2 days and then annealing at 500 °C for 2 h. Then, 1 g of TNPs was mixed with 100 mL of 10 M NaOH solution in a teflon-lined autoclave and hydrothermal treatment was done at 150 °C for 18 h. The resultant sodium titanate nanotubes were washed with distilled water and 0.1 M HCl until pH 7 which resulted in TNTs with high Na<sup>+</sup> content and until pH 4-5 before further washing to pH 7 which resulted in TNTs with negligible Na<sup>+</sup> content. Then, the TNTs were dried and annealed at 500, 700 and 800 °C for 2 h.

### Characterization of TNTs

The crystal structure of the TNTs were determined by X-ray diffraction (XRD) spectroscopy using Siemens Diffractometer D5000 with Cu-K $\alpha$  radiation of 0.154 nm and the reading was taken at 2 $\theta$  of 20-80°. The morphology of the nanotubes was characterized using

field emission scanning electron microscopy (FESEM), Zeiss Supra 35VP FESEM and transmission electron microscopy (TEM), JEOL-JEM 2100. The surface area and porosity of the catalysts were examined using Micromeritics 3Flex surface characterization with nitrogen adsorption-desorption measurement done at -196 °C.

### Photocatalytic Degradation Experiments

The measurement of the photocatalytic activities of the TNTs was done in a home-built reactor consisting of a magnetic stirrer, 12 W UV lamp emitting photons at maximum wavelength of 365 nm and a flask for holding the pollutant to be degraded. 250 mL of 15 mg/L paraquat dichloride solution was placed in the flask and 0.1 – 0.3 g of TNTs with high or low Na<sup>+</sup> were added to it. At first, the paraquat dichloride-TNTs suspension was magnetically stirred in the dark for 1 h to attain adsorption-desorption equilibrium. Then 4 mL sample was taken and analyzed using UV-Vis spectrophotometer, (UV-1601PC, Shimadzu). The value of concentration obtained was taken as the initial value. The suspension was illuminated and the reaction continued for 5 h. Samples were collected at regular intervals and analyzed as mentioned above.

## RESULTS AND DISCUSSION

### Crystal Structure of TNTs

XRD patterns of the synthesized TNTs containing high and low amounts of Na<sup>+</sup> ions are shown in Fig. 1 (a) and (b), respectively. It was observed that the TNTs containing high amount of Na<sup>+</sup> ions shown in Fig. 1(a) have lower crystallinity than TNTs with low Na<sup>+</sup> ions content shown in Fig. 1(b). According to Fig. 1(a) and 1(b), TNTs calcined at 500 °C showed tetragonal anatase phase of TiO<sub>2</sub> (JCPDS: 00-021-1272). Increasing the annealing temperature to 700 °C led to the evolution of tetragonal rutile TiO<sub>2</sub> (JCPDS: 01-073-1232) and monoclinic sodium titanium oxide, Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> (JCPDS: 01-073-1398) while some peaks due to anatase were still present. Further increment of the annealing temperature to 800 °C resulted in complete transformation of the anatase phase to rutile and Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> phases. It was reported that at temperatures higher than ~ 600 °C, anatase TiO<sub>2</sub> will be transformed to rutile (Nolan *et al.*, 2009; Hanaor and Sorrell, 2011; Reidy *et al.*, 2006). The sharpening of the peaks at 800 °C indicates higher crystallinity of the TNTs compared to when annealed at 500 and 700 °C. The Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> species present on the catalysts is due to the residual Na<sup>+</sup> ions from the hydrothermal treatment of TiO<sub>2</sub> with NaOH. Another remarkable difference in Fig. 1(a) and (b) is the intensity of peaks due to Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> species. Fig. 1(b) shows very low intensity of Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> peaks which indicated better removal of Na<sup>+</sup> ions compared to Fig. 1(a).

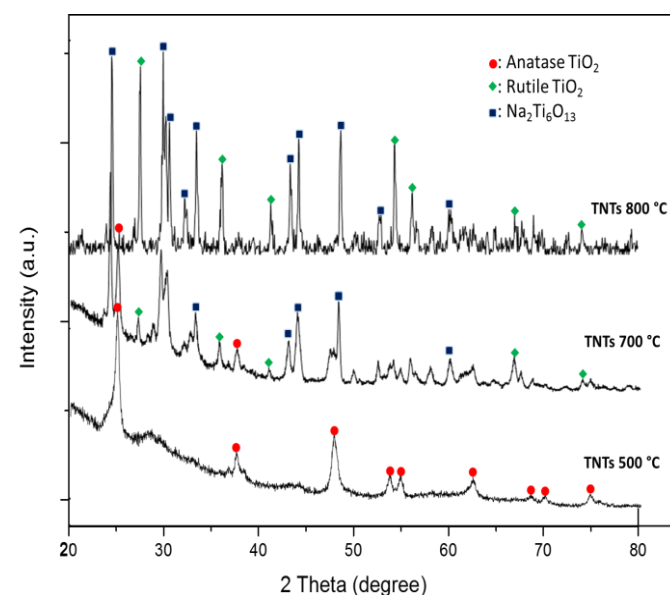


Fig. 1 (a) XRD patterns of TNTs with high Na<sup>+</sup> content.

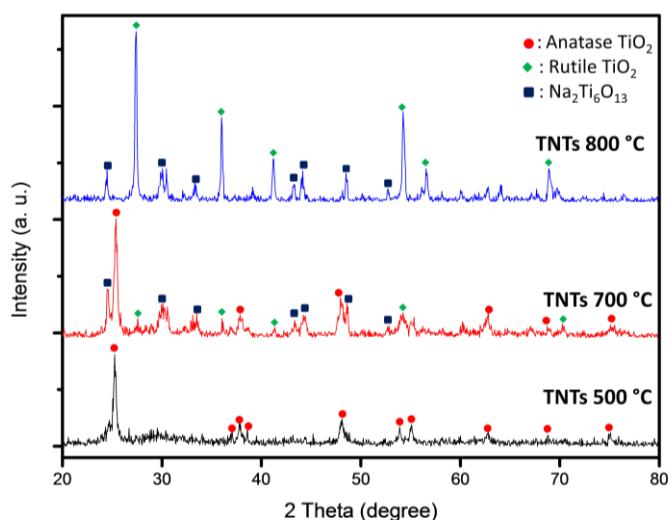


Fig. 1 (b) XRD patterns of TNTs with low  $\text{Na}^+$  content.

### Morphology of TNTs

The FESEM and TEM images of TNTs of TNTs with low  $\text{Na}^+$  ions content are presented in Fig. 2 confirm the formation of TNTs in this study. Fig. 2 (a), (b) and (c) show the FESEM images while Fig. 2 (d), (e) and (f) show the TEM images of TNTs annealed at 500, 600 and 800 °C for 2 h, respectively. The FESEM images in Fig. 2 (a-c) show a progressive increase in size as the annealing temperature increased from 500 to 800 °C. As can be observed in Fig. 2 (d), hollow multi-walled TNTs where obtained at 500 °C. Increasing the annealing temperature to 600 °C led to a reduction in the inner diameter as shown in Fig. 2(e). This must have resulted in a reduction in surface area from 49.5  $\text{m}^2/\text{g}$  to 23.5  $\text{m}^2/\text{g}$ . At 800 °C, the inner diameter of the TNTs tend to shrink completely and the TNTs were transformed into nanorods leading to the loss of surface area (Fig. 2(f)). The increase in size of the TNTs annealed at 800 °C is due to the growth of crystallites at this temperature. This is evident in the sharp reduction of surface area from 49.53  $\text{m}^2/\text{g}$  at 500 °C to 8.97  $\text{m}^2/\text{g}$  at 800 °C and the increase in crystallinity observed in the XRD result.

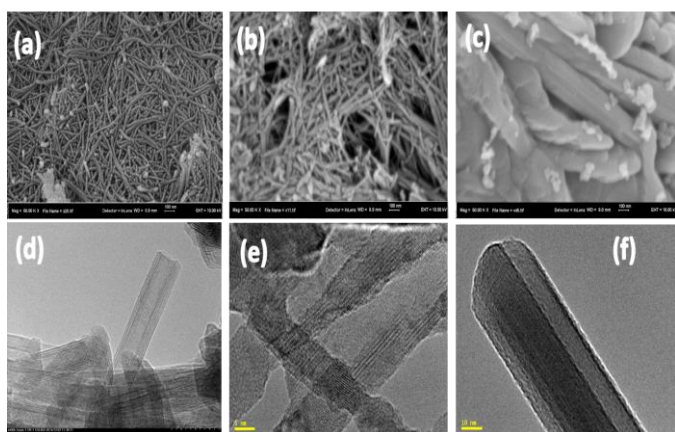


Fig. 2 FESEM images of TNTs annealed at (a) 500 °C, (b) 600 °C and (c) 800 °C and TEM images of TNTs annealed at (d) 500 °C, (e) 600 °C and (f) 800 °C.

### Textural Properties of TNTs

The surface area and porous structure of TNTs annealed at 500, 700 and 800 °C are given in Table 1. The nitrogen adsorption – desorption isotherms of TNTs annealed at 500, 700 and 800 °C are given in Fig. 3. The results shown here are those of TNTs with low  $\text{Na}^+$  ions content because from the single point surface area measurement, not much difference was observed in the surface areas of TNTs containing high or low amounts of  $\text{Na}^+$  ions. For example, in

the case of TNTs calcined at 500 °C, the surface areas obtained for samples with high and low  $\text{Na}^+$  ions content were 46.6 and 49.5  $\text{m}^2/\text{g}$ , respectively. This may be because the size of  $\text{Na}^+$  ions is not much bigger than the size of  $\text{H}^+$  ions. Thus, replacing  $\text{Na}^+$  with  $\text{H}^+$  only brought about a slight reduction in particle size. Thus, the isotherms given here are of TNTs with low  $\text{Na}^+$  ions content. As shown in Fig. 3, all the TNTs showed the type IV isotherm according to IUPAC classification which is characteristic of mesoporous materials (Sing, 1982). They exhibited type H3 hysteresis loop which is indicative of the presence of aggregates of particles forming slit-shaped pores (Tan et al., 2012; Leofanti et al., 1998). This is supported by the findings of other researchers who reported the type IV isotherms with type H3 hysteresis loop for TNTs (Song et al., 2010). As can be observed in Table 1, the surface area and pore volume decreased while the pore diameter increased with an increase in annealing temperature. This is also accompanied by thinning of the hysteresis loop. This observation can be attributed to the growth of crystallites and widening of pores as evidenced in the high crystallinity observed in XRD result and larger tube size observed in FESEM and TEM. (Górska et al., 2008).

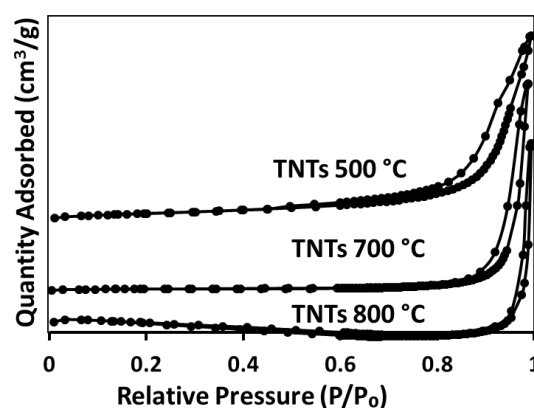


Fig. 3 Nitrogen adsorption-desorption isotherm of TNTs annealed at 500, 700 and 800 °C.

Table 1 Surface area, pore size and pore volume of TNTs calcined at 500, 700 and 800 °C.

Catalyst	BET surface area ( $\text{m}^2/\text{g}$ )	Langmuir surface area ( $\text{m}^2/\text{g}$ )	Pore diameter (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )
TNTs 500 °C	49.5291	63.1221	19.2406	0.3098
TNTs 700 °C	23.4985	28.8352	38.9845	0.2486
TNTs 800 °C	8.9697	9.5286	45.0238	0.0504

### Photocatalytic Testing

The result of photocatalytic screening of TNTs in the degradation of paraquat dichloride is presented in Fig. 4. TNTs containing high amount of  $\text{Na}^+$  ions showed very high adsorption capacity but exhibited poor photocatalytic activity at 500 °C achieving only 11.8% degradation of paraquat dichloride in 5 h. This may be because of the amorphous nature of  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  present which facilitated rapid  $e^-/\text{h}^+$  recombination. The  $\text{Na}^+$  ions tend to mask anatase  $\text{TiO}_2$  at low temperatures, thus preventing it from exerting its photocatalytic activity. The photocatalytic activity increased as the annealing temperature increased and at 700 °C, 43.3% degradation of paraquat dichloride was achieved. Furthermore, as the crystallinity increased at

high temperature of 800 °C coupled with the evolution of rutile phase TiO<sub>2</sub>, the photocatalytic activity increased considerably for the TNTs with high Na<sup>+</sup> content achieving 61.1% degradation of paraquat dichloride within 5 hr. This observation proves that there must be a balance between surface area and crystallinity of TNTs for efficient photocatalytic activity. Although, the TNTs calcined at 500 °C have higher surface area than those annealed at 800 °C, the amorphous Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> present served as sites for rapid e<sup>-</sup>/h<sup>+</sup> recombination. High crystallinity prevents rapid e<sup>-</sup>/h<sup>+</sup> recombination and is desirable for efficient photocatalytic activity (Yu et al., 2003). The mesoporous nature of the TNTs also assisted the adsorption of the pollutants and facilitated their degradation at the catalyst's surface.

On the other hand, TNTs with negligible Na<sup>+</sup> content demonstrated high photocatalytic activity at 500 °C achieving 74.9% degradation of paraquat dichloride within 5 h. This implies that it consisted mainly of anatase TiO<sub>2</sub> and the effect of rapid e<sup>-</sup>/h<sup>+</sup> recombination due to the presence of Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> has been overcome. This catalyst has also benefitted from the large surface area and pore volumes of the hollow nanotubes which aided the adsorption and subsequent degradation of paraquat dichloride. As the calcination temperature increased to 700 °C, 77.1% degradation of paraquat dichloride was achieved. This slight increase in activity may be due to the synergistic effects between the anatase and rutile species co-existing at this temperature (Scanlon et al., 2013). The surface area and mesoporous properties was still high enough to exert efficient photocatalytic activity. However, with further increase in annealing temperature to 800 °C, the photocatalytic activity dropped to 47.1%. This implies that the most active phase in the TNTs with low Na<sup>+</sup> content was anatase and as more anatase is being converted to rutile, the less the photocatalytic activity. More so, the drastic reduction in surface area and porosity might be another reason for the poor photocatalytic activity at this temperature.

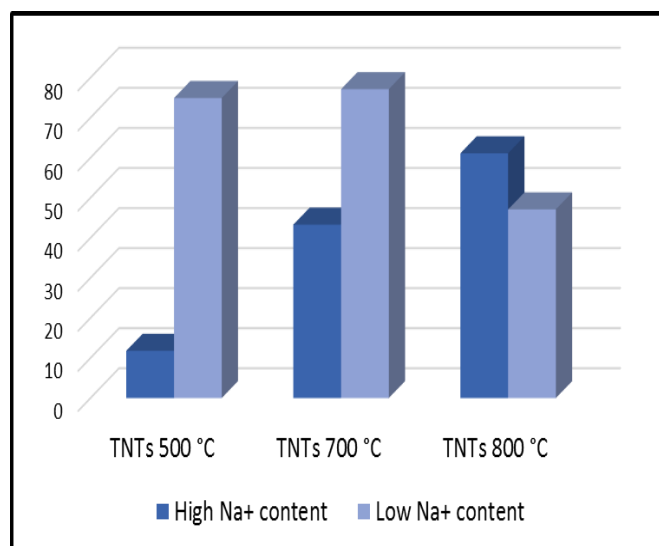


Fig. 4 Degradation efficiency of TNTs annealed at 500, 700 and 800 °C with high and low Na<sup>+</sup> content.

## CONCLUSION

The relationship between the photocatalytic properties of TNTs and their Na<sup>+</sup> ion content as a function of annealing temperature has been successfully established. TNTs with high Na<sup>+</sup> content exhibited poor performance at low annealing temperature due to the amorphous nature of Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> present and the photocatalytic activity increased with an increase in the annealing temperature. However, low or negligible Na<sup>+</sup> content favoured high photocatalytic activity of TNTs

at low to medium annealing temperature and experienced a reduction in activity at 800 °C. These observations showed that the amount of Na<sup>+</sup> ions in TNTs has significant effect on their crystal structure and hence their photocatalytic activities. Rutile TiO<sub>2</sub> was the most active phase in TNTs with high Na<sup>+</sup> content while anatase was the most active phase in TNTs with low Na<sup>+</sup> ions content.

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