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# Synthesis of $SiO_2/TiO_2$ nanocomposites under supporting of microwave with $SiO_2$ from RHA and its catalytic activity

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***ABSTRACT : In this work, $SiO_2/TiO_2$ nanocomposites have been successfully synthesized hydrothermal with rapid reaction time under supporting of microwave at power of 150 W, for 1 h using $SiO_2$ from rice husk ash (RHA) as silica source in Vietnam. The $SiO_2/TiO_2$ nanocomposites were characterized by UV–vis spectroscopy, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), transmission electron microscopy (TEM), fourier transform-infrared spectroscopy (FTIR), and X-ray diffraction (XRD). It was also demonstrated that the $SiO_2/TiO_2$ nanocomposites were extremely good catalytic activity and high stability. Our results show that $SiO_2/TiO_2$ nanocomposites were obtained with particle sizes in range from 10-30 nm and highly pure formed in 1 h. Moreover, the $SiO_2/TiO_2$ nanocomposites' stability increased to more than 24 h for investigating their catalytic activity in the saltwater medium with highly treatment efficiency respective about 66.4% and 75.2% under the lighting conditions of the sunlight and the UV-light in 3 h for comparisons.***

*Keywords:* RHA, $SiO_2/TiO_2$ nanocomposites, catalytic activity, microwave, sunlight, UV-light.

## 1. INTRODUCTION

In last years, titanium dioxide ($TiO_2$) nanomaterials have been widely studied because of their unique properties, various uses and multiple applications (i.e, in photocatalysis, air clean-up and water purification, optoelectronic devices, environment purification, photo-electrochemical solar energy conversion and optical coating, etc…) [1-9]. $TiO_2$ is one of the most promising materials for photocatalytic environmental applications in the form of anatase structure [10-12].

Moreover, $TiO_2$ is largely used as photocatalyst due to its beneficial properties, for example, high photocatalytic efficiency, physical and chemical stability, low cost and low toxicity [1-12].

In recent years, $TiO_2$-$SiO_2$ composite materials have been successful synthesized by sol-gel method; which could easy adjust on the structural and surface properties of the composite, to offer unique advantages for the preparation of highly dispersed tetrahedrally coordinated and transparent photocatalyst materials [13]. In the other hand, $TiO_2/SiO_2$ nanocomposites were synthesized by above methods with reaction time longer being ~10-16 h and high temperature over 100$^o$C.

$TiO_2/SiO_2$ composites are potential promising material in the field of heterogeneous photocatalysis, since they could provide simultaneously enhanced photocatalytic and thermal properties as compared to pure $TiO_2$ photocatalyst [14-17]. The photocatalytic activity and mechanical stability of $TiO_2/SiO_2$ nanocomposites were determined highly dependent on the Ti/Si ratios and improved by the addition of about 50% $SiO_2$ in the previous reports [18-22].

In this work, $SiO_2/TiO_2$ nanocomposites were synthesized by the green method under supporting of microwave with $SiO_2$ obtained from the extraction of rice husk ash (RHA) in Vietnam. The effect of reaction time on particle size, ratios of $SiO_2$:$TiO_2$ on catalytic activity, calcinations temperature and phase transformation of anatase to rutile $TiO_2$ were investigated. In addition, morphology and characterization of $SiO_2/TiO_2$ nanocomposites were determined by TEM, EDS, UV-vis, FTIR and XRD. Moreover, the catalytic activity of $SiO_2/TiO_2$ nanocomposites was also studied using the sunlight and the UV-light as an energy source to active their catalytic capacity in the salt solution used as the saltwater medium with highly treatment efficiency, leading to reduce amount of salt ions in the seawater and to transform the saltwater into the freshwater.

## 2. MATERIALS AND METHOD

### 2.1. Materials

Titanium dioxide ($TiO_2$) powder, 3-aminopropyl trimethoxysilane (APS: $C_6H_{17}NO_3Si$, 95%), amoniac solution ($NH_4OH$) were all purchased from Acros. All solutions were prepared using deionized water from a MilliQ system. Rice husk ash (RHA) was collected from Vinh Long province, then crushed and sifted to achieve raw materials' particle sizes ~160 □ m.

*Table 1.* Chemical composition of RHA

| Constituent | % Composition |
|---|---|
| $SiO_2$ | 87.9 |
| $Al_2O_3$ | 3.2 |
| $K_2O$ | 4.6 |
| CaO | 1.6 |
| MgO | 1.8 |
| $Fe_2O_3$ | 0.6 |

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| | |
|---|---|
| L.O.I | 0.3 |

*2.2. Method*

*2.2.1. Preparation of $SiO_2$ sol from RHA*

First step, rice husk ash (RHA) (24 g) was dispersed to 300 mL of NaOH solution (2M) under stirring for 30 min. And then, the solution was boiled under supporting of microwave at 150 W, for 1 h. The yellow aqueous solution (DD1) was obtained by filtration. Next step, the DD1 mixture was stirred and gradually dropped HCl solution (2 M) until the DD1 mixture precipitated and obtained a white solid of $SiO_2$ gel. Final, $SiO_2$ gel were collected by centrifugation, washed with distilled water (DI $H_2O$) and ethanol (ratio 1:1) about 3 times and diffused into 200 mL of DI $H_2O$ and ethanol with ratio 1:1 to obtain $SiO_2$ sol (DD2) more purity for the preparation of $SiO_2/TiO_2$ nanocomposites in next steps; and dried in oven at 80$^o$C for 12 h to determine the characterization of $SiO_2$ particles.

*2.2.2 Synthesis of $SiO_2/TiO_2$ nanocomposites*

40 mL of $SiO_2$ sol (DD2) obtained from RHA was added to 60 mL of ethanol aqueous under stirring at room temperature. The produced dispersion was treated by 200 □L $NH_4OH$ solution and stirred for 20 min at room temperature. After that, $TiO_2$ solution (i.e, various ratios about weight of $TiO_2$ powder (2.5; 1.43; 1.11; và 0.77 g) in ethanol (10 mL) were sequentlly added drop to the above $SiO_2$ solution and continuous stirred for 10 min at room temperature. Next, the mixture of $SiO_2/TiO_2$ solution (with different ratios between $SiO_2$:$TiO_2$ = 4:1; 7:1; 10:1; and 13:1, respectively) were sequential placed in a microwave oven at 150 W for 1 h. The resulting $SiO_2/TiO_2$ nanocomposite was centrifuged and washed with ethanol/acetone then dried at 80$^o$C in oven for 12 h. In order to study phase transformation of prepared nanocomposite, it is calcined for 2 h at 500 and 800$^o$C and the obtained samples were determined by XRD, respectively.

*2.2.3. Characterization techniques*

Spectroscopic analysis of the $SiO_2/TiO_2$ nanocomposite was performed using a Fourier transform infrared (FT-IR) spectrometer (Bruker Model-Vertex 70-Spectroscopy) and UV-vis spectrophotometer (Labomed Spectro UV-VIS UVD 3500). Phase identification of the $SiO_2/TiO_2$ nanocomposite was measured by X-ray diffraction (XRD) obtained on Philips X-pert diffractometer using Cu K□ (CuK-alpha) line radiation. The morphology of the $SiO_2/TiO_2$ nanocomposite was determined by a scanning electron microscope (SEM; S-4800 Hitachi) and transmission electron microscopy (TEM, Philips-EM208S electron).

*2.2.4 Preparation for investigating the catalytic activity of $SiO_2/TiO_2$ nanocomposites in the saltwater medium*

100 g of $SiO_2/TiO_2$ nanocomposites were added into 1000 mL of saltwater with concentration of 12.5‰. The mixture solution above (DD3 solution) was stirred for 30 min to ensure that the processing of saltwater's adsorption and desorption on the catalyst nanocomposites' surfaces reach equilibrium.

The catalytic activity of $SiO_2/TiO_2$ nanocomposite was performed by using the light conditions of the UV light and the sunlight. The DD3 solution was illuminated in different times respectively of 30; 60; 90; 120; 150; and 180 min using the UV light. The DD3 solution (100 mL) was taken out every time being 30 min, centrifuged and determined the salt's concentration in the solution after centrifuging by hydrometer. Furthermore, the $SiO_2/TiO_2$ nanocomposite's catalytic activity was also observed under the condition of the sunlight in the time range from 11:00 AM to 14:00 PM. This catalyst's preparation is the same process that for using of the UV light, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Morphology and optical absorption properties of $SiO_2/TiO_2$ nanocomposites

The UV-vis spectra of $SiO_2/TiO_2$ nanocomposites showed the maximum absorption peak at 239 nm. Figure 1 shows the solution absorbance spectra of $SiO_2/TiO_2$ nanocomposites prepared with $SiO_2$:$TiO_2$ weight ratios of 4:1; 7:1; 10:1; and 13:1. The absorption peak of $SiO_2/TiO_2$ nanocomposites was gradually increased intensity with increasing contents of $TiO_2$ (spectra (d)-(a) in Figure 1). Moreover, the energy level of $SiO_2$:$TiO_2$ nanocomposites at ratio of $SiO_2$:$TiO_2$ = 7:1 needs to provide energy for the electron conversion is lower than that of $SiO_2/TiO_2$ nanocomposites sample at ratio of $SiO_2$:$TiO_2$ = 4:1 and other samples for comparisons – see in Figure 1. Thus, $SiO_2/TiO_2$ nanocomposite sample with ratio of $SiO_2$:$TiO_2$ = 7:1 is the optimal sample, since the energy need to activate for the conversion of electron on this material was the lowest as compared to other samples, respectively – see in Figure 1.

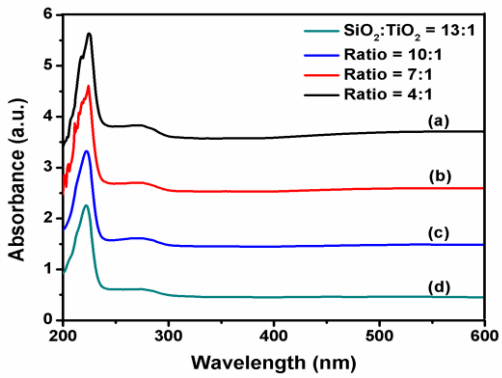


*Figure 1.* UV-vis spectra of $SiO_2/TiO_2$ nanocomposites with weight ratios of $SiO_2$:$TiO_2$ of (a) 4:1; (b) 7:1; (c) 10:1; and (d) 13:1.

FT-IR spectrum of the synthesized $SiO_2/TiO_2$ nanocomposites – see in Figure 2, show that three characteristic bands appeared at around 1200, 950 and 750 cm$^{-1}$. The absorption peaks (bands) around 750 and 1200 cm$^{-1}$ are representative of $TiO_2$ and $SiO_2$ matrixes in nanocomposite. The band at ~950 cm$^{-1}$ has been assigned to the stretching of the Si-O$^-$ species of Si-O-Ti or Si-O defect sites which are formed by the inclusion of $Ti^{4+}$ ions into the $SiO_2$ matrixes. Therefore, the appearance of the band at ~950 cm$^{-1}$ indicates that the $TiO_2$ particles are mounted into $SiO_2$ matrixes with $SiO_2/TiO_2$ nanocomposite. And the broad peak appearing at 3100-3500 cm$^{-1}$ is assigned to the feature stretching vibration of –OH groups which is further confirmed by the weak band at ~1642 cm$^{-1}$ [23, 24].

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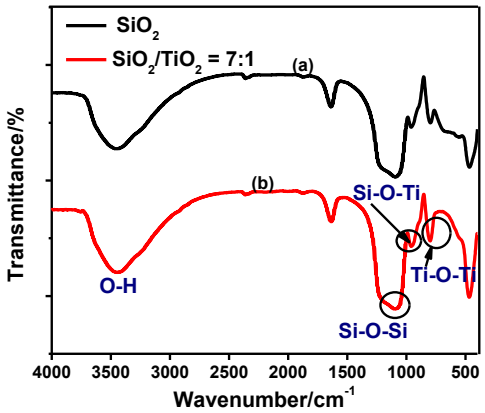


*Figure 2.* FT-IR spectrum of (a) $SiO_2$ powder and (b) $SiO_2/TiO_2$ nanocomposites.

X-ray diffraction pattern shows that the sample is characterized by an oval single peak with diffraction angle (2□ □ about 22° – 23° – see Figure 3(a), which shows amorphous structure of the synthesized $SiO_2$ [25]. As shown in Figure 3 (b-c), when $TiO_2$ sol was added into $SiO_2$ sol, leading to appear of the diffraction peaks at 2□ = 21.5° - 23° and 27.2°, which is characterizated for the amorphous structure of $SiO_2$ and the $TiO_2$ crystalline rutile phase, respectively [26]. Thus, It demonstrated that $TiO_2$ has a good adsorption on the $SiO_2$ substrate.

Figure 3 (b-c) show the resulting of XRD patterns of $SiO_2/TiO_2$ nanocomposite and calcined samples. It indicates that synthesized $SiO_2/TiO_2$ nanocomposite has crystalline anatase phase in amorphous silica matrix. The calcined $SiO_2/TiO_2$ nanocomposites at 800°C has transform from the amorphous silica to the crystobalite silica phase [27]. Doping of $TiO_2$ into $SiO_2$ could effectively retard the growth of nanoparticles and thus reduce the particle size. The particle size of $SiO_2/TiO_2$ composite calcined at 500 and 800°C are close together but 800°C a clear jump in the particle size is shown due to transformation of the amorphous silica to the crystobalite silica phase – see in Figure 3.

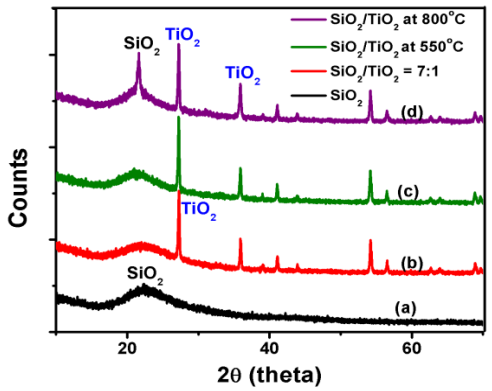


*Figure 3.* XRD patterns of (a) $SiO_2$ powder and (b) $SiO_2/TiO_2$ nanocomposites at 80°C and calcined composites: (c) 500°C and (d) 800°C with ratio of $SiO_2/TiO_2$ = 7:1.

From the resulting SEM image of $SiO_2/TiO_2$ nanocomposite shows in Figure 4, it indicates that surface of $SiO_2/TiO_2$ nanocomposites are porous structure and $TiO_2$ particles homogeneous distributed on the $SiO_2$ surface by silica mixtries. Moreover, the catalytic ability of the material depend on their morphology and surface area so much, as well as the small particle size of catalytic materials are better than that of bulk materials.

And the energy dispersive X-ray analysis (EDX) clearly shows the presence of Si, Ti, and O with weights of 34.29% Si, 7.22% Ti, and 58.50% O in the sample. It confirmed the formation of $SiO_2/TiO_2$ nanocomposites in the ratio of $SiO_2/TiO_2$ = 5:1 as shown in Figure 5, which is approximate with that ratio of original $SiO_2/TiO_2$ = 7:1.

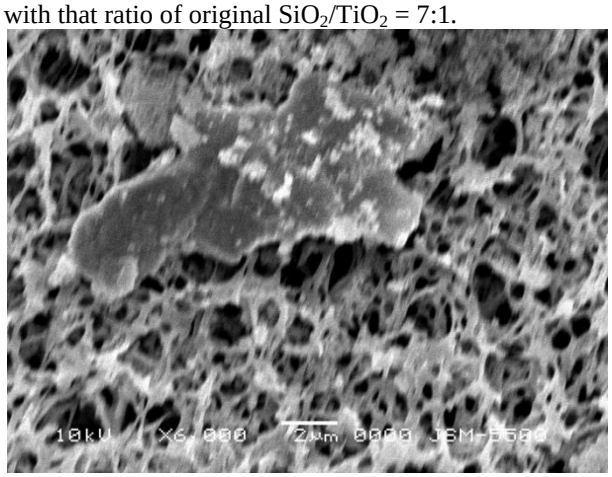

*Figure 4.* SEM image of $SiO_2/TiO_2$ nanocomposites at ratio of $SiO_2$:$TiO_2$ = 7:1.

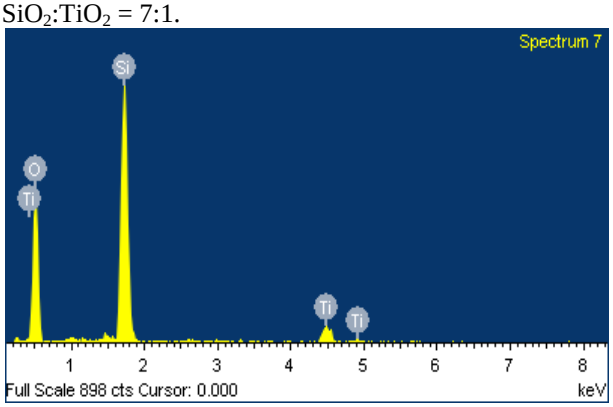


*Figure 5.* EDX spectrum of $SiO_2/TiO_2$ nanocomposites at ratio of $SiO_2$:$TiO_2$ = 7:1.

Figure 6 shows representative TEM image of $SiO_2/TiO_2$ nanocomposites sample. The image of the $SiO_2/TiO_2$ composites reveals that the nanosize. Here, $SiO_2/TiO_2$ nanocomposites (10-30 nm) were uniformly formed as shown in Figure 6. It demonstrated that the $SiO_2/TiO_2$ nanocomposite was synthesized by a simple method under supporting of microwave, which is seem as a green synthetic method beause of its environmental friendly, not expensive, and rapid reaction time, etc…

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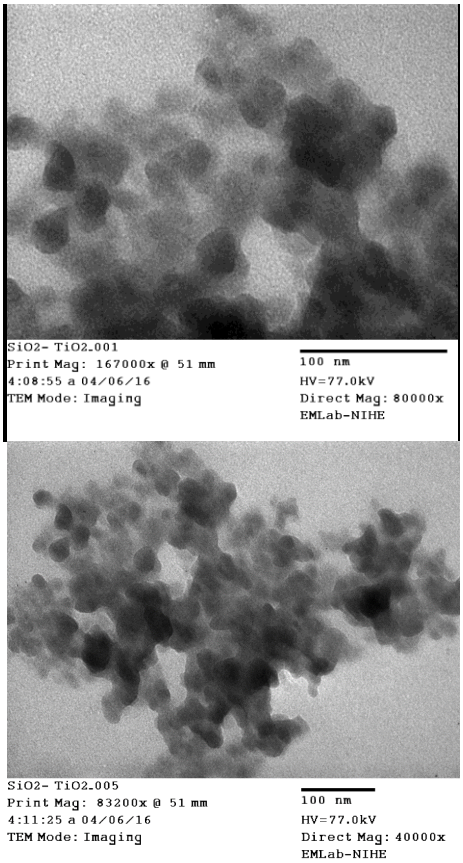


*Figure 6.* TEM image of $SiO_2/TiO_2$ nanocomposites at ratio of $SiO_2$:$TiO_2$ = 7:1.

3.2. Catalytic activity measurements

The catalytic activity of the synthesized $SiO_2/TiO_2$ nanocomposites were investigated by changes of the UV-vis absorption spectrum of $SiO_2/TiO_2$ nanocomposites after adsorption of metal ions (i.e, $Na^+$, $K^+$, etc...) in the salt solution as well as in the saltwater medium or in the seawater on the $SiO_2/TiO_2$ nanocomposites' surfaces under light conditions of the sunlight and the UV-light, respectively. Results show in Figure 7, it indicates that the treatment efficiency or adsorption efficiency of ions in the saltwater medium on the $SiO_2/TiO_2$ nanocomposite's surfaces under the lighting of the UV-light is 75.2% higher than that of the sunlight being ~66.4%, respectively.

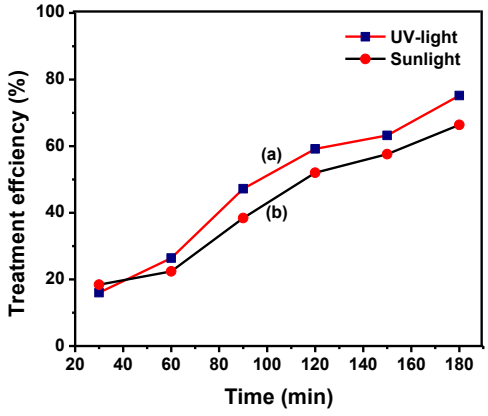


*Figure 7.* Treatment efficiency of $SiO_2/TiO_2$ nanocomposites in the saltwater medium using (a) the UV-light and (b) the sunlight

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4. CONCLUSION

In this study, we have successfully synthesized $SiO_2/TiO_2$ nanocomposite by green method under supporting of microwave in 1 h at 150 W with $SiO_2$ obtained from the extraction of rice husk ash (RHA) in Vietnam. Herein, $SiO_2/TiO_2$ nanocomposites have particle size around ~10-30 nm and their catalytic activity quite highly with the treatment efficiency respective ~75.2%; and 66.4% using the UV-light and the sunlight in 180 min for the adsorption of $Na^+$, $K^+$ ions in the saltwater medium on the $SiO_2/TiO_2$ nanocomposite's surfaces. Thus, $SiO_2/TiO_2$ nanocomposites are potential promising material applications in fields of treatment environment, photocatalytic, semiconductor devices due to their good catalytic activity, low cost and friendly environment.

REFERENCE

i. Visinescu C. M., Sanjines R., Levy F., Marcuc V. and Parvulescu V.I. - Tantalum Doped Titania Photocatalysts: Preparation by dc Reactive Sputtering and Catalytic Behavior. Journal of Photochemistry and Photobiology A:Chemistry 174 (2005) 106-110.

ii. Habibi M. H., Tangestaninejad S. and Yadollahi B. - Photocatalytic Mineralization of Mercaptans as Environmental Pollutants in Aquatic System Using TiO2 Suspension. Applied Catalysis. B: Environment 33 (2001) 57-61.

iii. Shchukin D. G. and Sviridov D. V. - PhotocatalyticProcesses in Spatially Confined Micro- and Nanoreactors. Journal of Photochemistry and Photobiology A:Chemistry Review 7 (2006) 23-39.

iv. Zhang R., Gao L. and Zhang Q. - Photodegradation of Surfactants on the Nanosized TiO2 Prepared by Hydrolysis of the Alkoxide Titanium. Chemosphere 54 (2004) 405-411.

v. Patterson K., Lykins B. W., Ireland J. C., Richardson S. D., Thruston A. D. and Collett T. W. - Identification of TiO2/UV Disinfection Byproducts in Drinking Water. Environmental Science and Technology 30 (1996) 3327-3334.

vi. Awati P. S., Awate S. V., Shah P. P. and Ramaswamy V. - Photocatalytic Decomposition of Methylene Blue Using Nanocrystalline Anatase Titania Prepared by Ultrasonic Technique. Catalysis. Communications 4 (2003) 393-400.

vii. Beydoun D., Amal R., Low G. and McEvoy S. - Role of Nanoparticles in Photocatalysis. Journal of Nanoparticle Research 1 (1999) 439-458.

viii. Prairie M. R., Evans L. R., Stange B. M. and Marlinez S. L. - An Investigation of TiO2 Photocatalysis for the Treatment of Water Contaminated with Metals and Organic Chemicals," Environmental Science and Technology 9 (1993) 27.

ix. Chenga P., Denga C., Gub M. and Dai A. X. - Effect of Urea on the Photoactivity of Titania Powder Prepared by Sol-Gel Method. Materials Chemistry and Physics 107 (2008) 77-81.

x. Hoffmann M.R., Martin S.T., Choi W.Y., Bahnemann D.W. - Environmental Applications of Semiconductor Photocatalysis. Chemical Reviews 95 (1995) 69-96.

xi. Fox M.A., Dulay M.T. - Heterogeneous photocatalysis. Chemical Reviews 93 (1993) 341-357.

xii. Linsebigler A.L., Lu G.Q., Yates J.T. - Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results. Chemical Reviews 95 (1995) 735-758.

xiii. Marugan J., Lopez M. - Photocatalytic Decolorization and Mineralization of Dyes with Nanocrystalline $TiO_2/SiO_2$ Materials. J. Ind. Eng. Chem. Res. 45 (2006) 8900-8908.

xiv. Calleja G., Serrano D. P., Sanz R. and Pizarro P. - Mesostructured SiO2-Doped TiO2 with Enhanced Thermal Stability Prepared by a Soft-Templating Sol-Gel Route. Microporous and Mesopororous Materials 111 (2008) 429.

xv. Garzella C., Comini E., Bontempil E., Deperol L. E., Frigeri C. and Sberveglieri G. - Nanostructured TiO2 and W: TiO2 Thin Films by a Novel Sol-Gel Processing for Alcohol Sensing Devices. Materials Research Society Symposium Proceedings 638 (2001) 111.

xvi. Wang Z., Helmersson U. and Kall P. - Optical Properties of Anatase TiO2 Thin Films Prepared by Aqueous Sol-Gel Process at Low Temperature. Thin Solid Films 405 (2002) 50-54.

xvii. Ivanova T., Harizanova A. and Surtchev M. - Formation and Investigation of Sol-Gel TiO2-V2O5 System. Materials Letters 55(2002) 327-333.

xviii. Dohshi S., Takeuchi M. and Anpo M. - Effect of the Lo cal Structure of Ti-Oxide Species on the Photocatalytic Reactivity and Photo-Induced Super-Hydrophilic Properties of Ti/Si and Ti/B Binary Oxide Thin Films. Catalysis Today 85 (2003) 199-205.

xix. Gonçalves R. R., Messaddeq Y., Atik M. and Ribeiro S. J. L. - Optical Properties of ZrO2, SiO2 and TiO2-SiO2 Xero gels and Coatings Doped with Eu3+ and Eu2+. Journal of Material Research 2 (1999) 11-15.

xx. Nishide T., Sato M. and Hara H. - Crystal Structure and Optical Property of TiO2 Gels and Films Prepared from Ti-Edta Complexes as Titania Precursors. Journal of Material Science 35 (2000) 465-469.

xxi. Cabrera S., El Haskouri J., Beltra'n-Porter A., Beltra'n-Porter D., Marcos M. D. and Amoro's P. - Enhanced Surface Area in Thermally Stable Pure Mesoporous TiO2. Solid State Science 2 (2000) 513-518.

xxii. Zhou L. , Yan S. , Tian B., Zhang J. and Anpo M. - Preparation of TiO2-SiO2 Film with High Photocatalytic Activity on PET Substrate. Materials Letters 60 (2006) 396-402.

xxiii. Habeeb G. A. and Mahmud H.B. - Study on properties of rice husk ash and its use as cement replacement material. Materials Research 13 (2010) 185-190.

xxiv. Trần Kim Tiên Phương. Phương pháp điều chế $SiO_2/TiO_2$ cho phản ứng quang hóa p-xylen trong pha khí. Đại Học Cần Thơ, 2008.

xxv. Mehran Riazian, ESMAEIL BIAZAR N.M. - Nano Structural Properties of $TiO_2$-$SiO_2$. Oriental Journal of Chemistry (2011) 903-910.

xxvi. [Musić S., Filipović-Vinceković N., and Sekovanić L., Precipitation of amorphous $SiO_2$ particles and their properties. Brazilian Journal of Chemical Engineering 28 (2011) 89-94.

xxvii. Agudo J., Grieken M., Lopez-Munoz J. And Marugan J. – A Comprehensive study of the synthesis, characterization and activity of $TiO_2$ and mixed $TiO_2/SiO_2$. Applied Catalysis A: General 312 (2006) 202-210.