



## Preparation of Nb<sub>2</sub>O<sub>5</sub>-Graphene Nanocomposites and Their Application in Photocatalytic Degradation of Organic Dyes

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### Nb<sub>2</sub>O<sub>5</sub>-Graphene 나노복합체의 제조 및 유기염료 광촉매 분해반응의 응용성에 관한 연구

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**ABSTRACT** : Niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) nanoparticles were synthesized using niobium (V) chloride and pluronic F108NF as the precursor and templating agent, respectively. The Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were placed in an electric furnace at 700 °C and calcined under Ar atmosphere for 2 h. The morphology, crystallinity, and photocatalytic degradation activity of the samples were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and UV-vis spectroscopy. The Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites acted as a photocatalyst in the photocatalytic degradation of organic dyes under 254 nm UV light; the organic dyes used were methylene blue (MB), methyl orange (MO), rhodamine B (RhB), and brilliant green (BG). The photocatalytic degradation kinetics for the aforesaid dyes were determined in the presence of the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites.

**요약** : Niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) 나노입자는 niobium (V) chloride 와 pluronic F108NF를 전구체와 주형체로 사용하여 합성하였다. Nb<sub>2</sub>O<sub>5</sub>-graphene 나노복합체는 아르곤 가스 분위기 전기로 조건에서 2시간 동안 700 °C로 가열하였다. 시료의 결정화도, 결정형태, 광촉매 분해 반응성은 X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV-vis spectroscopy를 사용하여 측정하였다. Nb<sub>2</sub>O<sub>5</sub>-graphene 나노복합체는 254 nm의 자외선 조건에서 유기염료 광촉매 분해 반응의 광촉매로 사용되었다. 유기염료는 methylene blue (MB), methyl orange (MO), rhodamine B (RhB), brilliant green (BG)이 사용되었다. 또한 Nb<sub>2</sub>O<sub>5</sub>-graphene 나노복합체를 사용하여 유기염료 광촉매 분해 반응의 반응 속도를 결정하였다.

**Keywords** : Niobium pentoxide nanoparticles, Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites, Photocatalytic degradation, Organic dyes, UV-vis spectroscopy.

## I. Introduction

Niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) is the most thermodynamically stable among niobium oxides.<sup>1</sup> Nb<sub>2</sub>O<sub>5</sub> nanoparticles act as an n-type transition metal oxide semiconductor with thermodynamic stability, chemical inertness, and low cytotoxicity.<sup>2,3</sup> Nb<sub>2</sub>O<sub>5</sub> nanoparticles have been used as effective catalysts in reactions regarding of pollution control, selective oxidation, hydrogenation/dehydrogenation, hydration/dehydration, electrochemical reaction, polymerization, and photocatalysis.<sup>4-11</sup> Despite the increasing interest in their applications in many technological fields, only a few studies have focused on Nb<sub>2</sub>O<sub>5</sub>

nanoparticles.<sup>12</sup>

Carbon is a wonder element because of its ability to form sp, sp<sup>2</sup>, and sp<sup>3</sup> hybridized orbitals; this characteristic allows carbon to form graphite, diamond, fullerene, and nanotube structures.<sup>13</sup>

Graphene is a monolayer of aromatic carbon atoms arranged in a honeycomb shape comprised of sp<sup>2</sup>-hybridized carbon atoms.<sup>14-16</sup> Graphene has received much attention because of its superior strength, electrical conductivity, and thermal conductivity.<sup>17,18</sup> These characteristics make graphene a good candidate material for field-effect transistors, solar cells, sensors, supercapacitors, composites, and transparent electrodes.<sup>19</sup>

Organic dyes are some of the main contaminants in wastewater, especially from laboratories, leather manufacturers, and

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textile factories.<sup>20, 21</sup> These organic dyes are harmful to humans and animals because of their genotoxic and carcinogenic properties.<sup>22, 23</sup> Photocatalysis, an advanced oxidation process (AOP), is one of the most popular wastewater treatment method.<sup>24</sup>

This paper discusses the technical information on the preparation and their applications of Nb<sub>2</sub>O<sub>5</sub> nanoparticles and Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites. The Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were heated and kept at 700 °C in an electric furnace under Ar atmosphere for 2 h.<sup>25</sup> UV-vis spectrophotometry was used to measure the photocatalytic effects of the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites on photocatalytic degradation of organic dyes under 254 nm UV light. The aim of this study was to investigate the photocatalytic degradation kinetics of organic dyes in the presence of hybrid nanocomposites.

## II. EXPERIMENT DETAILS

### 1. Chemicals

Niobium (V) chloride, methylene blue (MB), methyl orange (MO), rhodamine B (RhB), and brilliant green (BG) were purchased from Sigma-Aldrich. Acetic acid, hydrochloric acid, tetrahydrofuran (THF) and anhydrous ethanol were obtained from Samchun Chemicals. Pluronic F108NF was acquired from Kumkang Korea Chemical Co., Ltd. Graphene was supplied by ENano Tec.

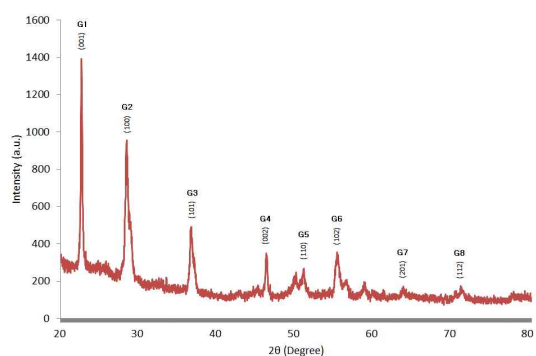
### 2. Instruments

The crystal structures of the Nb<sub>2</sub>O<sub>5</sub> nanoparticles, graphene, and Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were examined by X-ray diffraction (XRD, Bruker, D8 Advance) using Cu K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation. The morphology and particle size of the Nb<sub>2</sub>O<sub>5</sub> nanoparticles, graphene, and Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were examined using transmission electron microscopy (TEM, JEOL Ltd., JEM-2010) at an acceleration voltage of 200 kV. The surface of all Nb<sub>2</sub>O<sub>5</sub> nanoparticles, graphene, and Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites was examined by scanning electron microscopy (SEM, JEOL Ltd, JSM-6510) at an acceleration voltage ranging from 0.5 to 30 kV. UV-vis spectra of the samples were obtained using a UV-vis spectrophotometer (Shimadzu, UV-1601 PC). The samples were heat-treated in an electric furnace (Ajeon Heating Industry Co., Ltd).

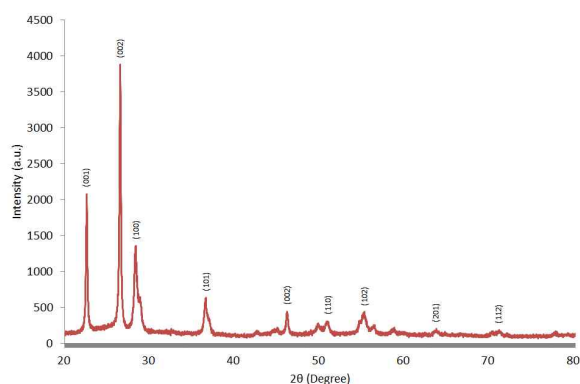
### 3. Synthesis

#### 3.1. Synthesis of Nb<sub>2</sub>O<sub>5</sub> nanoparticles

1.0 g of pluronic F108NF was dissolved in 5.0 mL of anhydrous ethanol. Then, 2.7016 g of niobium (V) chloride, 0.40 g of acetic acid, and 0.175 mL of hydrochloric acid were added



(a)



(b)

**Figure 1.** XRD patterns of the (a) synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles, (b) Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites.

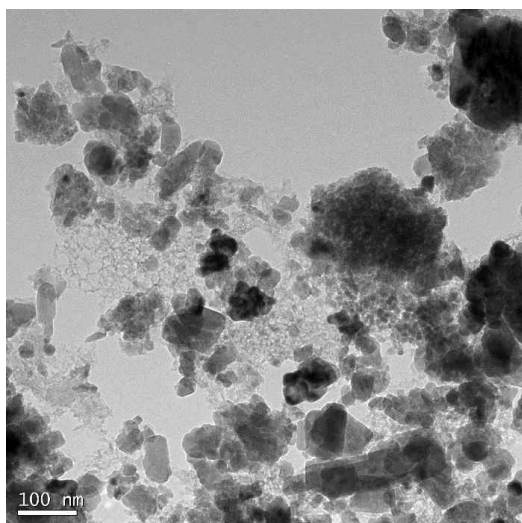
**Table 1.** Mean crystallite size of the synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles by Scherrer's formula.

Peak	2-Theta	FWHM	D (nm)
G1	22.66	1.2009	13.49
G2	28.41	1.319	12.43
G3	36.64	1.4962	11.19
G4	46.17	0.8071	21.40
G5	50.7	0.6693	26.27
G6	55.22	1.0631	16.87
G7	63.69	0.5512	33.93
G8	71.09	0.5118	38.15
Average			21.72

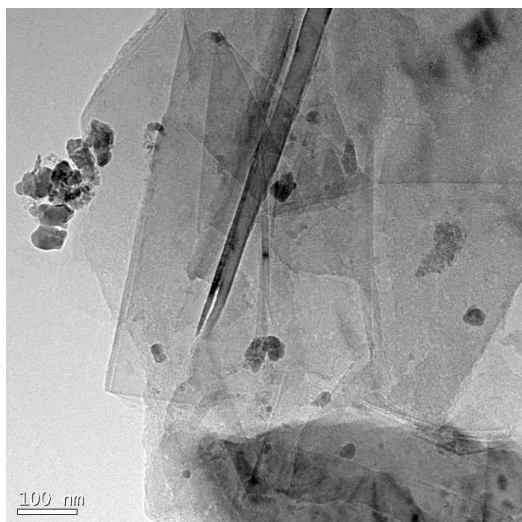
to the above solution under vigorous stirring. The solution sample gelatinized after being stored at 40 °C for 48 h. The obtained gel was calcined at 700 °C in an electric furnace under Ar atmosphere for 2 h, and finally the black powder of Nb<sub>2</sub>O<sub>5</sub> nanoparticles was prepared.

#### 3.2. Preparation of Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites

20 mg of the synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles and 20 mg of graphene were dissolved in 20 mL of tetrahydrofuran. After stirring for 60 min, the mixture was poured into a vessel and



(a)



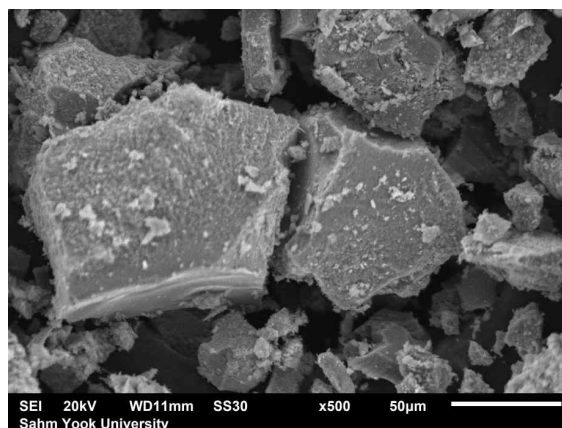
(b)

**Figure 2.** TEM images of the (a) synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles, (b) Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites.

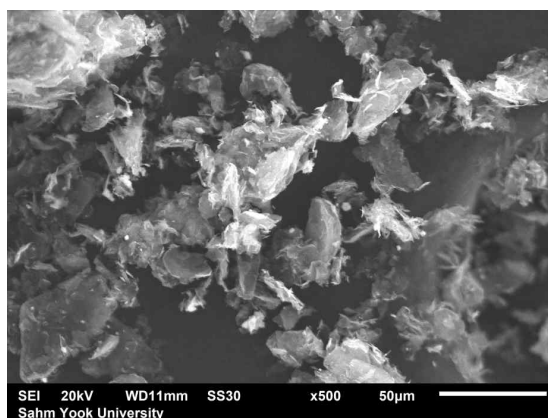
dried for 1 h to vaporize the organic solvent. The vessel was calcined at 700 °C in an electric furnace under Ar atmosphere for 2 h. Subsequently, the prepared Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were cooled to room temperature under Ar gas conditions for 5 h.

### 3.3. Evaluation of photocatalytic degradation of organic dyes with Nb<sub>2</sub>O<sub>5</sub> nanoparticles and Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites

The prepared Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were used as a photocatalyst for the degradation of organic dyes such as MB, MO, RhB, and BG. 5 mg of the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites was placed separately in a 10 mL vial containing 10 mL of the aqueous organic dye solution. Each vial containing the organic dye solution was irradiated with 254 nm UV



(a)



(b)

**Figure 3.** SEM images of the (a) synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles, (b) Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites.

light and the degradation data were collected using a UV-vis spectrophotometer.

### 3.4. Photocatalytic degradation kinetics of various organic dyes

The photocatalytic degradation kinetics of MB, MO, RhB, and BG in the presence of the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were determined by using the first-order reaction equation. The photocatalytic degradation kinetics for the organic dyes were calculated from experimental data using the software package Microsoft Excel (Version 2010) to obtain a linear regression curve.

## III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the (a) synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles and (b) Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites. The XRD peaks of the Nb<sub>2</sub>O<sub>5</sub> nanoparticles were observed at  $2\theta = 22.66^\circ, 28.41^\circ, 36.64^\circ, 46.17^\circ, 50.70^\circ, 55.22^\circ, 63.69^\circ,$  and  $71.09^\circ$ , which were assigned to the (001), (100), (101), (002), (110), (102), (201), and (112) planes<sup>26</sup>, respectively (figure

1 (a)). The XRD peaks of the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were observed at  $2\theta = 22.57^\circ, 28.34^\circ, 36.57^\circ, 46.10^\circ, 50.79^\circ, 55.24^\circ, 63.95^\circ,$  and  $70.95^\circ$  due to the Nb<sub>2</sub>O<sub>5</sub> nanoparticles, and at  $26.51^\circ$  due to graphene (figure 1 (b)).

Figure 2 shows TEM images of the (a) synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles and (b) Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites. The Nb<sub>2</sub>O<sub>5</sub> nanoparticles, which were triangular, rectangular, and quasi-spherical in shape, appeared to agglomerate. The size of the Nb<sub>2</sub>O<sub>5</sub> nanoparticles ranged from 20 nm to 70 nm. In the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites, the Nb<sub>2</sub>O<sub>5</sub> nanoparticles were placed above the graphene nanoparticles (figure 2 (b)). A comparison of figures 2 (a) and 2 (b) showed that after heat treatment, the Nb<sub>2</sub>O<sub>5</sub> nanoparticles in the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were broken into smaller parts.

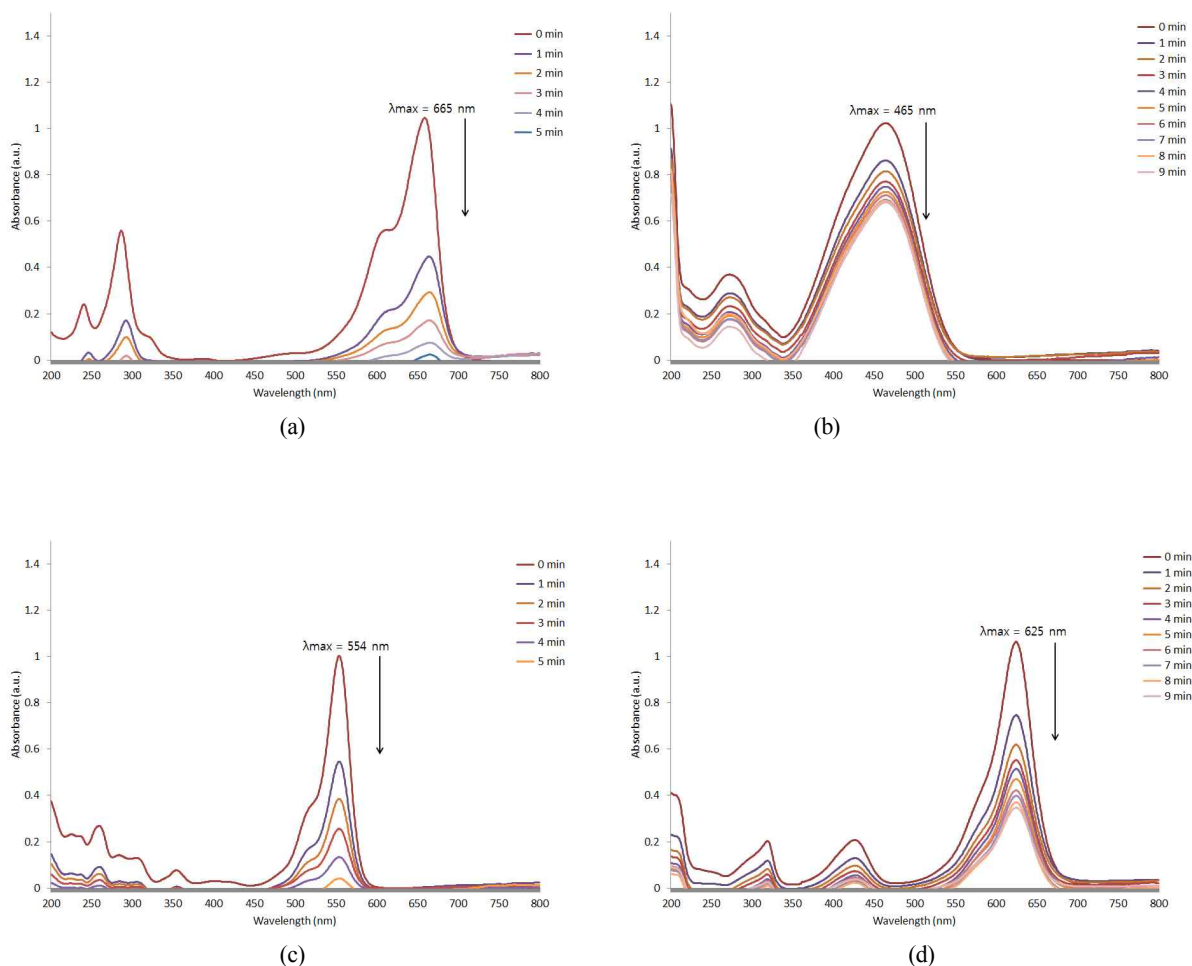
Figure 3 shows SEM images of the (a) synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles and (b) Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites. The SEM image of the Nb<sub>2</sub>O<sub>5</sub> nanoparticles revealed that they were shaped like stones (figure 3 (a)). In the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites, the Nb<sub>2</sub>O<sub>5</sub> nanoparticles were located above the graphene nanoparticles (figure 3 (b)). A comparison of figures

3 (a) and 2 (b) revealed the Nb<sub>2</sub>O<sub>5</sub> nanoparticles in the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites to be more collapsed than the synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles.

As a result of the heat treatment, the Nb<sub>2</sub>O<sub>5</sub> nanoparticles in the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were much smaller and had a larger surface area than the synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles.

Figure 4 depicts UV-vis spectra showing the degradation of (a) MB, (b) MO, (c) RhB, and (d) BG in the presence of the synthesized Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites under 254 nm UV irradiation for 1 min. The photocatalytic performance of the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites was superior for MB to for RhB, BG, and MO<sup>27</sup>. The order of effectiveness among the organic dyes degraded was MB > RhB > BG > MO.

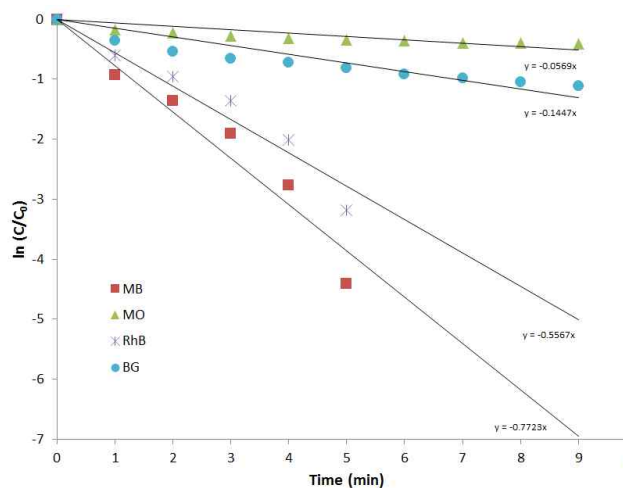
Figure 5 shows the kinetics of the photocatalytic degradation of MB, MO, RhB, and BG with the synthesized Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites under 254 nm UV irradiation. The time interval of the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites was a 1 min. The kinetics of the photocatalytic degradation of the dyes were calculated using the first-order equation, where C is the con-



**Figure 4.** UV-vis spectra of the degradation of (a) MB, (b) MO, (c) RhB and (d) BG with the synthesized Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites.

**Table 2. Kinetic data of the photocatalytic degradation of MB, MO, RhB and BG by first-order reaction which is kinetics equation with synthesized Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites.**

Time (min)	MB (lnC/C <sub>0</sub> )	MO (lnC/C <sub>0</sub> )	RhB (lnC/C <sub>0</sub> )	BG (lnC/C <sub>0</sub> )
0	0	0	0	0
1	-0.9282	-0.1727	-0.6073	-0.3524
2	-1.3558	-0.2275	-0.956	-0.5403
3	-1.9049	-0.283	-1.3663	-0.6535
4	-2.7663	-0.312	-2.014	-0.7253
5	-4.4113	-0.342	-3.189	-0.8138
6		-0.364		-0.923
7		-0.3904		-0.9793
8		-0.3977		-1.0533
9		-0.4077		-1.1189



**Figure 5.** Kinetics of the degradation of (a) MB, (b) MO, (c) RhB and (d) BG with the synthesized Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites.

centration at a certain time in the degradation,  $C_0$  is the initial concentration,  $k$  is the apparent first-order rate constant, and  $t$  is the reaction time. Table 2 lists the kinetic data of the photocatalytic degradation of MB, MO, RhB, and BG, as determined using the first-order reaction equation. The photocatalytic degradation rate for the organic dyes followed the order MB > RhB > BG > MO.

## IV. CONCLUSIONS

The Nb<sub>2</sub>O<sub>5</sub> nanoparticles were triangular, rectangular, and quasi-spherical with diameters ranging from 20 nm to 70 nm. The Nb<sub>2</sub>O<sub>5</sub> nanoparticles in Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites were located above the graphene nanoparticles. As a result of heat treatment, the Nb<sub>2</sub>O<sub>5</sub> nanoparticles in the Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites had larger surface areas and were smaller than the synthesized Nb<sub>2</sub>O<sub>5</sub> nanoparticles. The average crystallite size of the Nb<sub>2</sub>O<sub>5</sub> nanoparticles was 21.72 nm, as determined using Scherrer's equation. Among the organic dyes tested, MB showed the maximum degradation in the presence of the synthesized Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites as a photocatalyst. The reaction rate calculated using first-order kinetics for the photocatalytic degradation of the organic dyes in the presence of the synthesized Nb<sub>2</sub>O<sub>5</sub>-graphene nanocomposites was the highest for MB, followed by RhB, BG, and MO.

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