Better adsorption capacity of SnO$_2$ nanoparticles with different graphene addition

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Abstract. The adsorption capacity of SnO$_2$ nanoparticle has been studied by graphene and nanographene platelets (NGP) additions using co-precipitation method. The crystalline phase, composition, and morphology of the samples are analyzed using X-Ray Diffraction (XRD), Energy Dispersive X-Ray (EDX), Fourier Transform Infrared Spectroscopy (FT-IR), and Transmission Electron Microscope (TEM). Tetragonal structure of SnO$_2$ is shown for the nanoparticle and its composites. The presence of graphene and NGP is also confirmed. The adsorption capacity of the nanoparticle and its composites are analyzed by observing the degradation of methylene blue (MB) as the organic dye model using UV-Vis Spectroscopy. The result shows that SnO$_2$ composite with graphene achieves higher adsorption capacity of about 20% than the composite with NGP. The fitting of equilibrium adsorption capacity result indicates that the adsorption mechanism of SnO$_2$ composite with graphene tends to follow the Langmuir adsorption-isotherm model.

1. Introduction
Environmental pollution has become a major attention in recent years. One of the major concerns of researchers is water pollution due to industrial dye wastes. A great number of industries use dyes in their products: food, clothing, paper, pharmaceuticals, cosmetics and textiles [1,2]. The existence of dye in waste water, even in low concentration may be very dangerous for human’s life and microorganism [3]. Methylene blue (MB) is a type of dye materials which is important and has broad application in chemical analysis for pH indicator, dye for cellulose and bacteria dyes, and culture media for bacteria [4]. Therefore, various researches have been conducted and developed to settle problems being faced due to the use of this dye.

Various methods such as adsorption, coagulation and flocculation, oxidation, and chemical precipitation have been reported as the methods used to overcome issues of water pollution due to dye wastes. Of the various methods, adsorption is considered to be the best method because of its low cost, easily to be applied, and its availability of adsorbents [5]. Nanostructure material has been known to be able to become a good adsorbent because of its large surface area [6]. One of nanomaterials that is widely used in the degradation process of dye wastes is tin oxide (SnO$_2$). SnO$_2$ has various advantages such as its sensitivity when exposed to light and thermal energy, its numbers of intrinsic defect in its structure caused by low formation energy and strong attraction between the tin sites and oxygen vacancies [7]. In recent years, the graphene materials draw special attention to scientist in the world because of its unique properties such as its large surface area, its hydrophlicity, its high dispersibility, and its high mobility of charge electron [8]. Several reviews mention that graphene materials can be used as adsorbent in degrading dye wastes [9]. Therefore, considering the advantages of SnO$_2$ and graphene materials to be
applied in adsorption methods for waste water treatment, these two materials are combined to degrade dye wastes through adsorption process which is expected to get a better efficiency in degrading dye wastes than when each applied separately.

In this study, SnO$_2$ nanoparticle will be combined with two different types of graphene namely Nanographene platelets (NGP) and graphene, SnO$_2$/NGP and SnO$_2$/graphene that are applied as adsorbents to degrade dye and the adsorption mechanism of these two composites is also studied.

2. Experimental

2.1. Chemicals

All the reagents used are analytical grade and without going through further purification; tin chloride (SnCl$_2$), sodium hydroxide (NaOH), and ethanol. Nanographene platelets and graphene were bought from Angstrom Material.

2.2. Preparation SnO$_2$ nanoparticles

SnO$_2$ nanoparticles were synthesized using the modification method reported by Yue Li et al [10]. First, SnCl$_2$ is dissolved into ethanol and aquades, then NaOH solution is poured into the solution then stirred magnetically. This mixed solution is then heated at 180 °C for 3 hours, and cooled down at the room temperature. The deposit produced is centrifuged and rinsed using aquades and ethanol several times. The deposited particle is dried out under vacuum condition at 80 °C. SnO$_2$ nanoparticle is obtained after going through the calcination process for 3 hours at the temperature of 700 °C.

2.3. Preparation SnO$_2$/NGP and SnO$_2$/graphene composites

SnO$_2$/NGP is synthesized using the co-precipitation method. First, NGP is dissolved into aquades and ethanol through ultrasonic treatment for 2 hours, then SnO$_2$ nanoparticles is poured into the solution and stirred magnetically. The mixed solution is then heated at 120 °C for 3 hours. The result of solution is then centrifuged and dried at 70 °C under vacuum condition. The same method is also applied to synthesize SnO$_2$/graphene.

2.4. Characterizations

The samples are characterized using X-Ray Diffraction (XRD), measured using Rigaku Miniflex 600, while the image of transmission electron microscopy (TEM) is recorded using Tecnai G2 Supertwin. The spectrum of infrared absorption from the samples is obtained using Shimadzu FTIR spectrophotometer in the range of 400-4000 cm$^{-1}$, and the elements of the nanoparticle and composites are revealed using energy dispersive X-Ray (EDX) with the energy range of 0-5 keV.

2.5. Adsorption processes

Adsorption experiment is carried out by mixing SnO$_2$, SnO$_2$/NGP, and SnO$_2$/graphene into methylene blue (MB) solution used as pollutant model with the concentration of 20 mg/L, and the pH solution is adjusted using NaOH. The concentration of dye is analyzed using UV-Vis Spectrometer. Furthermore, adsorption experiment is carried out again with varying MB concentration for sample with best adsorption activity.

3. Results and Discussion

Figure 1 indicates the XRD pattern of SnO$_2$ nanoparticles, SnO$_2$/NGP and SnO$_2$/graphene composites. The diffraction pattern of the samples is observed at 2θ = 26.5°, 33.8°, 38°, 39°, 51.8°, 54.8°, 58°, 62°, 64.7°, 65.8°, 71.2°, 78.2°, 81.2°, 83.7° which indicates the existence (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202), (321), (400), (222) planes of the SnO$_2$ tetragonal structure. The peak at 2θ of 26.0° indicates (002) plane of the NGP structure. For graphene, there is only a broad peak at around 2θ of 25°, which indicates the structure of graphene. The diffraction peaks of SnO$_2$, NGP and graphene at SnO$_2$/NGP and SnO$_2$/graphene composites are overlapped at 2θ of around 26°. The grain
size is calculated using the Scherrer’s formula, and the lattice parameter is calculated using Rietveld refinement method that is used in MAUD software. The calculation results of grain size and lattice parameter is presented in Table 1.

The FTIR spectrum of SnO₂ nanoparticles, SnO₂/NGP and SnO₂/graphene composites are presented in figure 2. Figure 2a shows the FTIR spectra for SnO₂/NGP composites, while the FTIR spectra for SnO₂/graphene composites is shown in figure 2b. The absorption of SnO₂ nanoparticle appears in the range of 540-660 cm⁻¹ which indicates O-Sn-O and Sn-O stretching vibration modes. The absorptions in range of 3400 cm⁻¹ and 1634 cm⁻¹ indicate the O-H group stretching and bending vibration modes originating from water molecule [11] while absorption in the range of 1220 cm⁻¹ and 1527 cm⁻¹ indicates the C-OH and C-O stretching vibration modes [12,13]. All SnO₂, NGP and graphene characteristics can be revealed with the FTIR spectrum of SnO₂/NGP and SnO₂/graphene.

### Table 1. Lattice parameter and grain size of SnO₂, SnO₂/NGP and SnO₂/graphene

| Sample          | Lattice Parameter (Å) | <D> (nm) |
|-----------------|-----------------------|----------|
|                 | a=b=c                 | a=b=c    |
| SnO₂            | 4.7384                 | 3.1872   | 44       |
| SnO₂/NGP        | 4.7442                 | 3.1891   | 3.6382   | 33       |
| SnO₂/graphene   | 4.7586                 | 3.1994   |          | 21       |

![XRD Spectrum](image1.png)  
**Figure. 1.** XRD Spectrum of SnO₂ nanoparticle, SnO₂/NGP and SnO₂/graphene composites

![FTIR Spectrum](image2.png)  
**Figure. 2.** FTIR Spectrum of SnO₂ nanoparticle, SnO₂/NGP and SnO₂/graphene composites
The Energy Dispersive X-Ray (EDX) spectrum of SnO$_2$ nanoparticles, SnO$_2$/NGP and SnO$_2$/graphene composites are shown in figure 3. Based on the EDX measurement results, the SnO$_2$ nanoparticle consists of Sn, O and Cu elements. The energy spectra of Cu presents in the results of EDX measurements for the use of copper grid as the sample holder. The existence of NGP and graphene in the SnO$_2$/NGP and SnO$_2$/graphene composites are confirmed with the existence of carbon energy spectra in the EDX measurement results. The absence of other elements in the EDX spectrum showed the absence of an impurity in SnO$_2$ nanoparticle and composites samples.

The morphology of SnO$_2$ nanoparticles, SnO$_2$/NGP and SnO$_2$/graphene composites is analyzed using Transmission Electron Microscope (TEM). The TEM result of these samples is indicated in figure 4. Figure 4a is the morphologic image of SnO$_2$ nanoparticle in irregular shape with the average particle size of 40-50 nm. When NGP and graphene are incorporated in SnO$_2$ nanoparticle, the morphology of the produced composites is still in irregular shape, but smaller particle size with the average particle size of 30-36 nm for SnO$_2$/NGP (figure 4b) and 18-25 nm for SnO$_2$/graphene (figure 4c). Appearance of fine wrinkled structure in these figures indicate the presence of NGP and graphene in SnO$_2$/NGP and SnO$_2$/graphene composites samples. The results of TEM image confirm the grain size calculation results from the XRD measurements (Table 1). The clear of TEM images indicates good crystal characteristics [17].

MB degradation process of SnO$_2$ nanoparticles, SnO$_2$/NGP and SnO$_2$/graphene composites is shown in figure 5. Figure 5a is the process of decolorization (color change) from MB during the adsorption process using SnO$_2$ nanoparticles and composites. It can be seen that the decolorization process increases simultaneously with addition of NGP dan graphene from 22% for SnO$_2$ nanoparticles and 35% and 60%
respectively for SnO$_2$/NGP and SnO$_2$/graphene composites. To identify the adsorption capability of the adsorbent to adsorb the pollutants on its surface per unit of time, there is a certain contact time during an adsorption process [14]. Figure 5b indicates the adsorption capacity against time up to 250 minutes. It can be seen that the adsorption capacity of the SnO$_2$ nanoparticles and composites nearly reach the equilibrium at 180 minutes referred to equilibrium adsorption capacity. Based on the adsorption result, the highest equilibrium adsorption capacity is reached by SnO$_2$/graphene at 39.1 mg/g then followed by
SnO$_2$/NGP at 25.9 mg/g and SnO$_2$ nanoparticles at 19.2 mg/g. Figure 6a shows the adsorption capacity of SnO$_2$/graphene composites to degrade varied MB initial concentrations. In this study, MB concentration is varied from 20 mg/L – 150 mg/L with the adsorbent dosage of 0.3 g/L. The figure shows an increase of total adsorption capacity of SnO$_2$/graphene as the MB concentration is increased with equilibrium adsorption capacity reach its maximum of 80.17 mg/g. The adsorption mechanism of SnO$_2$/graphene can be identified using two adsorption models namely Langmuir and Freundlich [12-13]. The Langmuir adsorption-isotherm model indicates monolayer coverage on the surface of adsorbent, while the Freundlich adsorption-isotherm model indicates a heterogeneous system [15-16]. The experimental data of the adsorption capacity are fitted using Langmuir and Freundlich adsorption-isotherm models (figure 6b and 6c). It can be seen that the experimental data are more closely fitting using the Langmuir adsorption-isotherm model ($R^2=0.99$) than using the Freundlich adsorption-isotherm model ($R^2=0.95$).

3. Conclusion
The SnO$_2$ nanoparticles, SnO$_2$ composites with NGP and graphene addition have been successfully synthesized using co-precipitation method. The XRD spectrum of the SnO$_2$ nanoparticle and composites show the tetragonal structure of SnO$_2$. The spectrum of EDX confirm the existence of NGP and graphene in SnO$_2$ composites and also confirms the absence of impurity in the samples. The equilibrium adsorption capacity of SnO$_2$ nanoparticles and composites reach the value of 19.2, 25.9 and 39.1. The equilibrium adsorption capacity value increases with the presence of NGP dan graphene in SnO$_2$ composites and the best adsorption capacity is obtained by SnO$_2$/graphene. The adsorption process of SnO$_2$/graphene follows the Langmuir adsorption-isotherm model.

4. Reference
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