Preparation of TiO$_2$-ZnO and its activity test in sonophotocatalytic degradation of phenol

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Abstract. Synthesis of TiO$_2$-ZnO and its activity test in Sono photocatalysis degradation of phenol has been conducted. The synthesis was performed by the sol-gel mechanism by using titanium isopropoxide and zinc acetate as precursors with the Ti: Zn ratio of 5:1. Characterization of material were conducted by x-ray diffraction analysis, surface area analysis and also diffuse reflectance UV-Visible spectrophotometry. The material obtained from the synthesis was tested in photocatalysis, Sono catalysis and Sono photocatalysis degradation of phenol solution. Results showed that material exhibited the activity of varied mechanism o-phenol degradation. In advance, the Sono photocatalysis degradation produced the synergy index of 1.169 compared to both photocatalysis and Sono catalysis.

1. Introduction
In recent years, photocatalytic degradation processes of the organic contaminant with ultraviolet (UV) radiation over semiconductor photocatalyst like titanium dioxide (TiO$_2$) and zinc oxide (ZnO) have gained interest as an effective water purification method. The effectivity of the process in decomposing target molecules by mineralizing toxic content is the positive aspect compared to the previous method of water purification such as adsorption. The important goal of these processes was to change the toxic dyes into harmless end products than original compounds. For these purposes, a comprehensive review of the UV assisted heterogeneous photocatalytic oxidation process revealed that the combination of both TiO$_2$ and ZnO can produce rapid degradation and potentially attain full mineralization of the organic contaminants under mild reaction conditions such as ambient pressure and temperature. Furthermore, due to the ability of semiconductor TiO$_2$ and ZnO to catch energy from ultrasonic wavelength, Sono catalysis degradation also becomes an opportunity in effort to find the new effective technique of degradation[1]. The recent experimental investigations have showed that toxic compounds can be degraded by coupled advanced oxidation processes via the exciting of powerful like hydroxyl radicals (•OH). Beside of photochemistry, sonochemistry is one of the important processes for this similar scheme. Sonolysis involves the use of ultrasonic waves for the production of cavitations bubbles. The pyrolysis in the cavitation of bubbles, as well as the generated hydroxyl radicals that required to, oxidizes the targeted organic compounds.

The formation of TiO$_2$ and ZnO in TiO$_2$-ZnO composite is widely investigated for such application of photocatalysis and also sonocatalysis [2] [3,4]. Several investigation reported the feasibility of TiO$_2$-ZnO in producing photoactive material for compounds degradation. From previous works the activity of in photocatalysis and Sono catalysis can create the synergistic effect by the combined photocatalytic and Sono catalytic methods called as sonophotocatalysis [5,6]. Phenol degradation was chosen as reaction model to evaluate the effect of each process for the activity of the
catalyst in Sono photocatalysis was studied. The work is aimed to evaluate the synthesis of TiO$_2$-ZnO material and study the effectiveness of Sono photocatalytic compared to Sono catalysis and photocatalysis process by the prepared catalyst.

2. Materials and method

2.1. Materials

The following chemicals were used: titanium (IV)-isopropoxide (TTIP, 97%, Aldrich, Germany), zinc acetate dihydrate, isopropanol, and phenol were purchased from Merck-Millipore, Germany.

2.2. Instrumentation

The physicochemical character of prepared TiO$_2$-ZnO was studied by x-ray diffraction (XRD) measurement, surface area analysis and scanning electron microscope-energy dispersive x-ray (SEM-EDX0. The x-ray diffraction (XRD Philips) analysis was performed by using Ni-filtered Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. The diffraction patterns were taken over a 20 range from 3-65°. Surface morphology was recorded by scanning electron microscope SEM (Zeiss Ultra plus 40) while specific surface area analysis, pore volume, and pore radius determination were obtained by measurement with NOVA 2000e instrument.

2.3. Synthesis

Synthesis of TiO$_2$-ZnO was prepared by sol-gel method. A solution of titanium isopropoxide in isopropanol: water (1:1) solvent was titrated slowly by zinc acetate solution under stirring until the mole ratio of Ti: Zn = 5:1 with the addition of acetic acid of 0.5N. The mixture was then stirred for a night. A suspension obtained was then evaporated, dried and calcined at 400 °C for 4 h. As reference materials, a metal oxide of TiO$_2$ and ZnO were also prepared from the same precursors. TiO$_2$ was prepared by diluting titanium isopropoxide solution in isopropanol: water:1:1 and slowly added with acetic acid 0.5 N. The mixture was then stirred for 4 h. The obtained gel was then dried in an oven for a night before calcination at 400 °C for 4 h. Similar method was applied for ZnO synthesis by using zinc acetate dehydrate precursor. Both methods are in the presence of acetic acid as a hydrolyzing agent, and the calcination temperature is also 400 °C for 4 h.

2.4. Activity Test

Activity test experiments were conducted by phenol degradation solution. A solution of phenol with the concentration of 10 mg/L were prepared in distilled water and were mixed with prepared TiO$_2$-ZnO at the ratio of 500 mL phenol solution:0.25g TiO$_2$-ZnO taken in the reactor. The degradation experiments consist of varied mechanisms, i.e., Adsorption in which the material was mixed with phenol solution under stirring, without UV irradiation, without sonication. Photolysis in which the phenol solution was treated with stirring, with UV irradiation, without sonication. Photocatalysis in which the material was mixed with phenol solution under stirring and UV irradiation, without sonication. Sonocatalysis in which the material was mixed with phenol solution under stirring, without UV irradiation, with sonication. Sonophotocatalysis in which the material was mixed with phenol solution under stirring, with UV irradiation, with sonication.

2.3. Experimental Setup

The photocatalytic and Sono photocatalytic experiments were carried out in a photoreactor. An immersion well type photoreactor made of Pyrex glass set with a magnetic bar in the reactor on the magnetic stirrer for continuous agitation. UV light provided by 40 watts bulb (Philips) placed at 30
cm on top of the photoreactor. Ultrasound compartment for Sono catalysis and Sono photocatalysis was assembled by using Neytech sonicator operated at a frequency of 35 kHz and output power of 300 W.

Treated solution was analyzed by gas chromatography and chemical oxygen demand measurement. The COD determination tests were performed according to standard dichromate method using COD digester. The photodegradation efficiency was calculated with equation (1).

$$\eta = \frac{COD_i - COD_f}{COD_i} \times 100$$

(1)

where $\eta$ is the degradation efficiency, COD$_i$ is the initial chemical oxygen demand, COD$_f$ is the chemical oxygen demand of treated solution. A variation of phenol concentration and also a time of treatment were also performed in this study.

3. Result and Discussion

![XRD pattern of TiO$_2$-ZnO](image)

Figure 1. XRD pattern of TiO$_2$-ZnO

From XRD analysis, it is concluded that composite material of TiO$_2$-ZnO consists of TiO$_2$ in anatase and ZnO in wurtzite which those phases are also found in pure TiO$_2$ and ZnO. Reflection at $2\theta = 31.91^\circ$ and $36.41^\circ$ are correspond to wurtzite phase (JCPDS 36–1451), while anatase phase is identified by reflections at : $25.3^\circ$, $37.8^\circ$, $48.0^\circ$, $54.5^\circ$ (JCPDS 21-1272). The formation of wurtzite phase is related to that under normal conditions; wurtzite ZnO is thermodynamically stable compared to
cubic and another phase. The wurtzite phase also gives higher photoactivity (3.4eV) compared to cubic one (2.7 eV).

Figure 2. SEM images of the prepared materials

The surface profile of materials (Figure 2) exhibits the difference in surface morphology of TiO$_2$-ZnO compared to TiO$_2$ and ZnO. ZnO shows the aggregation of granules while TiO$_2$ has a smaller size of particles and TiO$_2$-ZnO express the combination of ZnO and TiO$_2$ morphologies. Furthermore, surface parameters consisting of specific surface area, pore volume and pore radius are other parameters required in both Sono catalysis and photocatalysis. The N$_2$ adsorption-desorption profile of prepared materials is presented in Fig.2, and calculated parameters are listed in Table 1. Adsorption-desorption pattern also indicates that the adsorption-desorption pattern of TiO$_2$-ZnO lies between the pattern of TiO$_2$ and ZnO. TiO$_2$ and TiO$_2$-ZnO obey type III in IUPAC classification while ZnO fit to type IV correspond to the small adsorbate-absorbent interaction potentials (similar to type III), and are also associated with pores in the 1.5 – 100 nm range.

Table 1. Surface parameter from N$_2$ adsorption-desorption analysis

| Parameter                        | TiO$_2$-ZnO | TiO$_2$ | ZnO  |
|----------------------------------|-------------|---------|------|
| BET surface area (m$^2$/g)       | 91.05       | 66.54   | 36.89|
| Single point surface area (m$^2$/g) | 88.51       | 45.46   | 21.76|
| t-plot external surface area (m$^2$/g) | 92.15       | 59.17   | 32.22|
| Pore Size (Å)                    | 14.99       | 11.05   | 15.09|
| Pore Volume (cc/g)               | 0.341       | 0.289   | 0.198|
| Edge wavelength (nm)             | 389.05      | 389.05  | 392.00|
| Band gap energy (eV)             | 3.19        | 3.19    | 3.16 |
Band gap energy is an important parameter in both Sono catalysis and photocatalysis. The measurement of band gap energy was conducted by DRUV-Vis, and the spectra are presented in Figure 3. The spectra exhibited the edge wavelength correspond to band gap energy values tabulated in Table 1. TiO$_2$-ZnO expressed the same band gap energy value with TiO$_2$ material which is 3.19 eV while ZnO shows the value of 3.16 eV. The same values of TiO$_2$-ZnO with TiO$_2$ is probably due to the domination of TiO$_2$ in TiO$_2$-ZnO in which the mole ratio of Ti: Zn is equal to 5:1.
The catalytic activity of the material in the varied process; photocatalysis, Sono catalysis and Sono photocatalysis of phenol degradation are determined by the reduction of phenol content and chemical oxygen demand (COD). Chromatogram of treated phenol solution by varied treatment is depicted in Figure 4. Phenol in solutions is approximated from the peak at the retention time of 0.456 min. From the chromatogram, it is noted that all treatment give less phenol in solution as showed by the lower peak height/area. Compared to adsorption, Sono catalysis, photocatalysis and also Sono photocatalysis give specific pattern in that new peaks identified. New peaks are the indication of new products from the catalytic reaction which is not from adsorption process. Phenol reduction and $\eta$ parameters obtained by varied treatment using varied catalysts is depicted in Figure 5.
From the data it is concluded that COD reduction is in line with phenol reduction. From various treatment the data imply that COD reduction is related to the less molecules to oxidize in treated solution especially from the Sono photocatalysis treatment. As reported in many works on photocatalytic degradation of phenol, the oxidation occurs by the following mechanism (equation (2-5)).

\[
\begin{align*}
\text{Photocatalyst} & \rightarrow h^+ + e^- \\
H_2O + h^+ & \rightarrow \cdot OH + H^+ \\
O_2 + e^- & \rightarrow \cdot O_2^- \\
\cdot O_2^- + H^+ & \rightarrow \cdot HO_2
\end{align*}
\]

The results show that in the presence of TiO₂-ZnO the combination of light and sound (Sono photocatalysis) enhances the degradation of phenol significantly. In the case of Sono catalysis, the degradation is 37.66% during 1 h while from photocatalysis, the degradation is 47.82%. However, Sono photocatalysis resulted in this research is approx. 99.31% degradation. From data in Table 2.

**Table 2. Phenol reduction and η of various process using varied materials**

| Process                  | TiO₂-ZnO | TiO₂ | ZnO |
|--------------------------|----------|------|-----|
| Phenol reduction (%)     | η        | Phenol reduction (%) | η          | Phenol reduction (%) | η          |
| Adsorption               | 50.28    | 49.5 | 40.28 | 39.5                  | 20.55 | 28.89 |  |
| Photocatalysis           | 47.82    | 68.99 | 47.02 | 56.89                  | 39.72 | 44.89 |  |
| Sonolysis + UV (w.o catalyst) | 61.45    | 72.7 | 56.45 | 61.47                  | 46.45 | 61.47 |  |
| Sonocatalysis            | 37.66    | 67.16 | 29.66 | 17.16                  | 24.66 | 17.16 |  |
| Sonophotocatalysis       | 99.99    | 89.31 | 90.99 | 79.91                  | 80.99 | 79.91 |  |

Thus, it is evident that the degradation of phenol under UV-light and ultrasound irradiation is more than the sum of degradation under individual photocatalysis and Sono catalysis process, thereby showing a synergistic effect. Effect of the presence of TiO₂-ZnO as a catalyst within the synergistic process is also indicated by the higher degradation efficiency of Sono photocatalysis than that of the treatment by using UV irradiation and sonication without a catalyst. The synergy index in the case of both catalyzes is calculated from the rate of degradation using the following equation (6).

\[
\text{Synergy index} = \frac{R_{\text{sonophotocatalysis}}}{R_{\text{sonocatalysis}} + R_{\text{photocatalysis}}}
\]
both mechanisms, the synergistic of Sono catalysis process, is higher compared to the photocatalysis. Physico-chemical character data listed in Table 1 suggest that the contribution of band gap energy rather than a specific surface area of the catalyst. From both Sono catalysis and photocatalysis, photocatalysis is more dominant compared to Sono catalysis as indicated by the higher phenol reduction efficiency.

![Figure 6](image.jpg)

**Figure 6.** Phenol reduction efficiency over TiO$_2$, ZnO and TiO$_2$-ZnO catalyst

4. Conclusion

TiO$_2$-ZnO catalyst was successfully prepared and found to be active in Sono catalytic, photocatalytic and also Sono photocatalytic degradation of phenol. Synergistic effect of Sono catalysis and photocatalysis is indicated by the synergistic index of Sono photocatalysis equal to 1.169.

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