

Full Length Research Paper

Solar photocatalytic degradation of phenol using nanosized ZnO and α -Fe₂O₃

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This work focuses on the solar photocatalytic degradation of phenol using nanosized ZnO and α -Fe₂O₃ synthesized via precipitation route. The synthesized ZnO and α -Fe₂O₃ were characterized using XRD, UV/Vis and surface area analysis. α -Fe₂O₃ was found to exhibit better solar photocatalytic activity than ZnO under identical experimental conditions due to the larger surface area and low band gap of α -Fe₂O₃. The photocatalytic degradation of phenol follows pseudo-first order kinetics on both ZnO and α -Fe₂O₃.

Key words: Photocatalysis, solar, phenol, ZnO, α -Fe₂O₃.

INTRODUCTION

Photocatalysis involves the use of semiconductors and electromagnetic radiation especially in the visible and ultraviolet regions to drive various photochemical processes (destruction of a wide variety of organic and inorganic pollutants and microorganisms, generation of hydrogen gas from water, etc). Some of the major advantages of photocatalysis include: ambient operating temperature and pressure conditions, low cost of photocatalysts, complete destruction of water pollutants and pathogens without generation of secondary pollutants, possibility of using solar energy to drive the process, etc. (Chong et al., 2010; Fujishima et al., 2007).

The photocatalytic activities of various semiconducting materials (TiO₂, ZnO, Fe₂O₃, CdS, GaP, ZnS, etc) and their composites to mineralize a wide variety of water pollutants have been investigated by many researchers. TiO₂ and ZnO are the most widely used photocatalyst due to their good photocatalytic activity, non-toxicity and low cost. ZnO was found to be more photocatalytically active than TiO₂ under solar irradiation (Hayata et al., 2011). The major disadvantage of TiO₂ and ZnO is their large band gap of about 3.2 eV (~388 nm) which makes

them effective only in the presence of UV light with wavelengths shorter than 380 nm (Casbeer et al., 2012). On the other hand, α -Fe₂O₃ as a visible light active photocatalyst with a bandgap of about 2.2 eV has been applied for photocatalytic degradation of a wide range of pollutants (Jaafar et al., 2012; Bakardjieva et al., 2007). Solar energy has the highest potential of all the renewable energies especially in tropical Africa (Blanco et al., 2009). Most developing countries have problems of wastewater management. Fortunately, there are high levels of solar radiation in most of these countries. Hence, there is the need to develop materials that can harness solar energy and use it to solve the problems of wastewater treatment. Phenol and its derivatives are found in the effluents of various industries such as petrochemical, coal, pharmaceutical, wood, paint, pulp and paper industries (Ahmaruzzaman, 2008). Phenol is easily absorbed through human skin causing skin and eye burns upon contact. Phenol affects the liver, kidneys, lungs, and vascular system. Excessive exposure to phenol may cause comas, convulsions, cyanosis and even death (Ahmaruzzaman, 2008).

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Photocatalytic degradation of phenolic compounds by various photocatalysts has been reported by several researchers (Hayata et al., 2011; Chiou et al., 2008; Valenzuela et al., 2002). For example, Valenzuela et al. (2002) investigated photocatalytic degradation of phenol and found ZnO to be more active than α -Fe₂O₃ under artificial ultraviolet illumination. The aim of this work was to synthesize nanosized ZnO and α -Fe₂O₃ using precipitation route and compare their effectiveness for solar photocatalytic degradation of phenol under identical experimental conditions.

MATERIALS AND METHODS

Synthesis and characterization of ZnO and α -Fe₂O₃

Analytical grade reagents purchased from a local chemical store in Zaria, Kaduna State, Nigeria were used throughout the work. 13.75 g of zinc nitrate was dissolved in 250 ml of deionized water. 13.85 ml of ammonium hydroxide was added at a constant rate to the solution with vigorous stirring at 50°C and a pH of 8. The formed precipitate was aged for 24 h, washed with deionized water and then filtered under vacuum. The product was dried overnight in an oven at 110°C. The dried product was further calcined in a furnace at 1000°C for 4 h to yield ZnO.

38.45 g of iron nitrate was dissolved in 250 ml of deionized water. 21 ml of ammonium hydroxide was then added. The mixture was stirred at 50°C and a pH of 8.0 for 3 h. The formed precipitate was aged for 24 h, washed with deionized water and then filtered under vacuum. The product was dried overnight in an oven at 110°C. The dried product was further calcined in a furnace at 1000°C for 4 h to yield α -Fe₂O₃.

X-ray diffraction (XRD) patterns of the synthesized ZnO and α -Fe₂O₃ were recorded using a powder X-ray diffractometer (Shimadzu, model 6000) employing Cu K α radiation source ($\lambda=0.154$ nm). Absorption spectra of the synthesized ZnO and α -Fe₂O₃ were recorded using a UV/Vis spectrophotometer (Jenway 6405). The specific surface area of the photocatalyst was obtained using a modified BET method which is based on the adsorption of water molecules on the surface of solid samples (Adefila et al., 2003).

Photocatalytic experiments

The concentration of phenol solution used in all the experiments was 500 mg/L. The pH of the solution is 4.0. 100 ml of phenol solution was mixed with 0.1 g of the photocatalyst (ZnO or α -Fe₂O₃) in the photoreactor and magnetically stirred for 2 h in the dark in order to establish adsorption-desorption equilibrium of phenol on the photocatalyst. Thereafter, the mixture was exposed to sunlight under continuous stirring at room temperature (28±2°C) for 6 h. After every hour, samples were taken for analysis after separating the photocatalyst particles. These samples were analyzed for residual concentration of phenol at 270 nm using a UV/Vis spectrophotometer (Jenway, 6405). The experiments were performed between 10 am to 4 pm in September, 2012. Experiments were repeated in duplicate for getting the reproducibility of results. The percentage photodegradation of phenol was calculated using Equation 1:

$$\text{Degradation} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

Where C_0 and C_t are the initial concentration of phenol and the concentration of phenol after irradiation time (t) respectively.

RESULTS AND DISCUSSION

Characterization of the synthesized ZnO and α -Fe₂O₃

The XRD patterns of the synthesized ZnO and α -Fe₂O₃ are displayed in Figures 1 and 2, respectively. In Figure 1, diffraction peaks were observed at $2\theta = 24.3^\circ, 33.3^\circ, 35.7^\circ, 40.9^\circ, 49.5^\circ, 54.1^\circ, 62.5^\circ$ and 64.0° . These peaks are similar to the typical peaks of the hematite phase of Fe₂O₃ with rhombohedral symmetry (JCPDS file No 33-0664). In Figure 2, diffraction peaks were observed at $2\theta = 31.75^\circ, 34.42^\circ, 36.24^\circ, 47.53^\circ, 56.58^\circ, 62.84^\circ$ and 67.91° . These peaks are similar to the typical peaks of the wurtzite phase of ZnO (JCPDS file No 33-0664).

The crystallite sizes of ZnO and α -Fe₂O₃ were determined using the Debye-Scherrer equation (Equation 2).

$$\tau = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

Where τ is the particle size, λ is the wavelength of the X-ray radiation (Cu K $\alpha = 0.1542$ nm), k is the shape factor ($k = 0.94$), β is the full line width at half maximum height and θ is the angular position of the peak maximum. The estimated crystallite sizes of ZnO and α -Fe₂O₃ were 58.4 nm and 58.2 nm, respectively. Hence, the synthesized ZnO and α -Fe₂O₃ are nanoparticles because their crystallite sizes are less than 100 nm. The UV-Vis absorption spectra of the catalysts are shown in Figure 3. ZnO absorption is exclusively in the ultraviolet region. Whereas, α -Fe₂O₃ exhibit broad absorption band that extends to the visible region (up to about 550 nm). The specific surface areas of ZnO and α -Fe₂O₃ were 39.5 m²/g and 162.3 m²/g, respectively, as determined by the modified BET method.

Photocatalytic degradation of phenol over ZnO and α -Fe₂O₃

Control experiments were performed by mixing 0.1 g of the synthesized photocatalyst (α -Fe₂O₃ or ZnO) with 100 ml of phenol solution in the dark. The results show that 6 h of adsorption of phenol in the dark on both ZnO and α -Fe₂O₃ resulted in the removal of less than 12 % of phenol. In the absence of photocatalyst (photolysis), the percentage degradation of phenol was only 21% in an irradiation time period of 6 h. The effect of irradiation time on the percentage degradation of phenol over ZnO and α -Fe₂O₃ as well as in the absence of photocatalyst is depicted in Figure 4. The percentage degradation of phenol increased with increase in the irradiation time, and

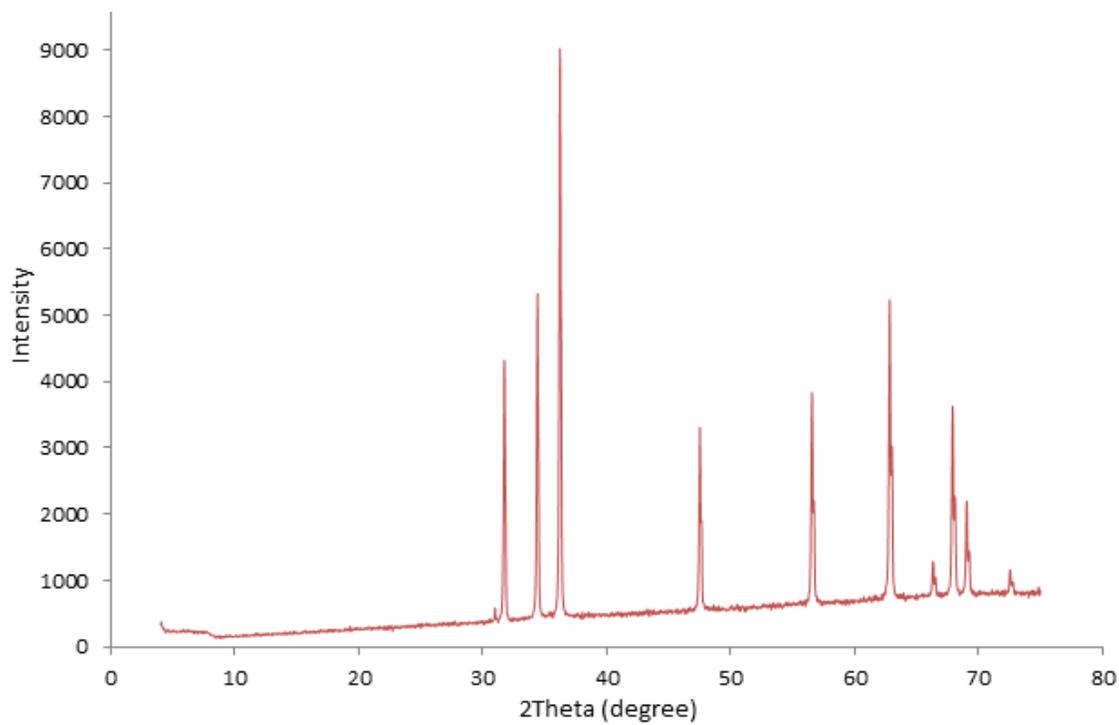


Figure 1. XRD pattern of the synthesized ZnO.

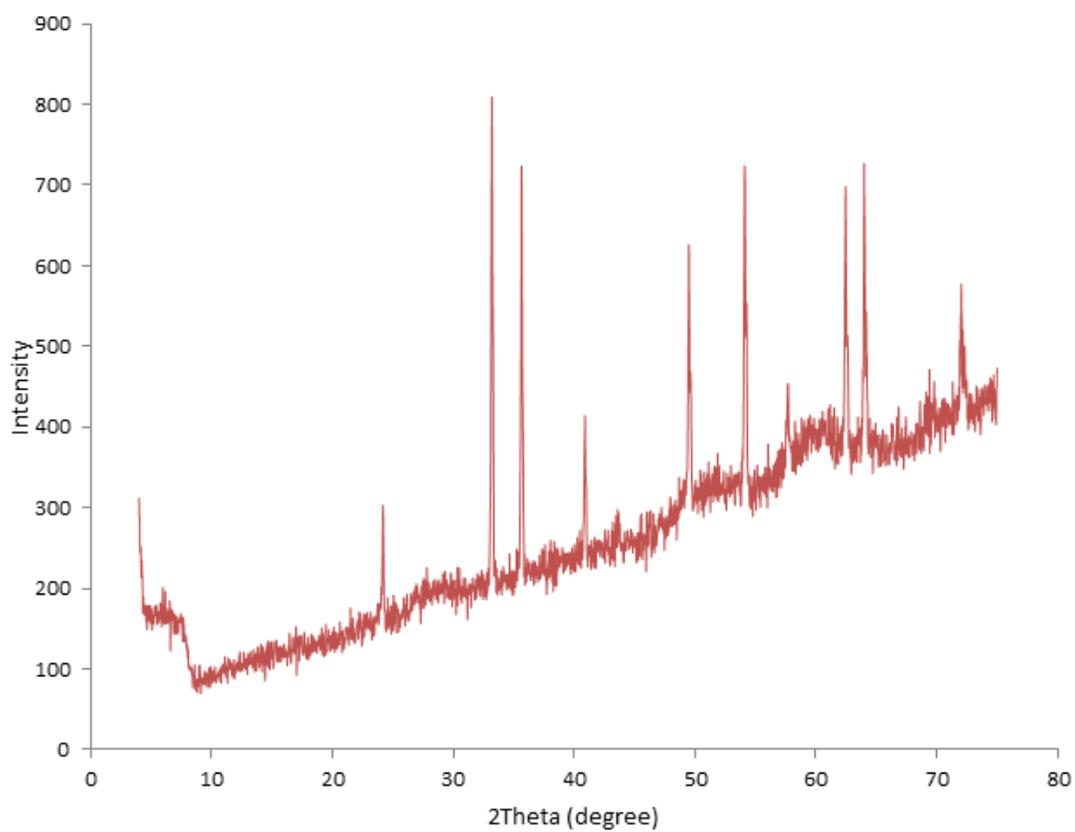


Figure 2. XRD pattern of the synthesized α -Fe₂O₃.

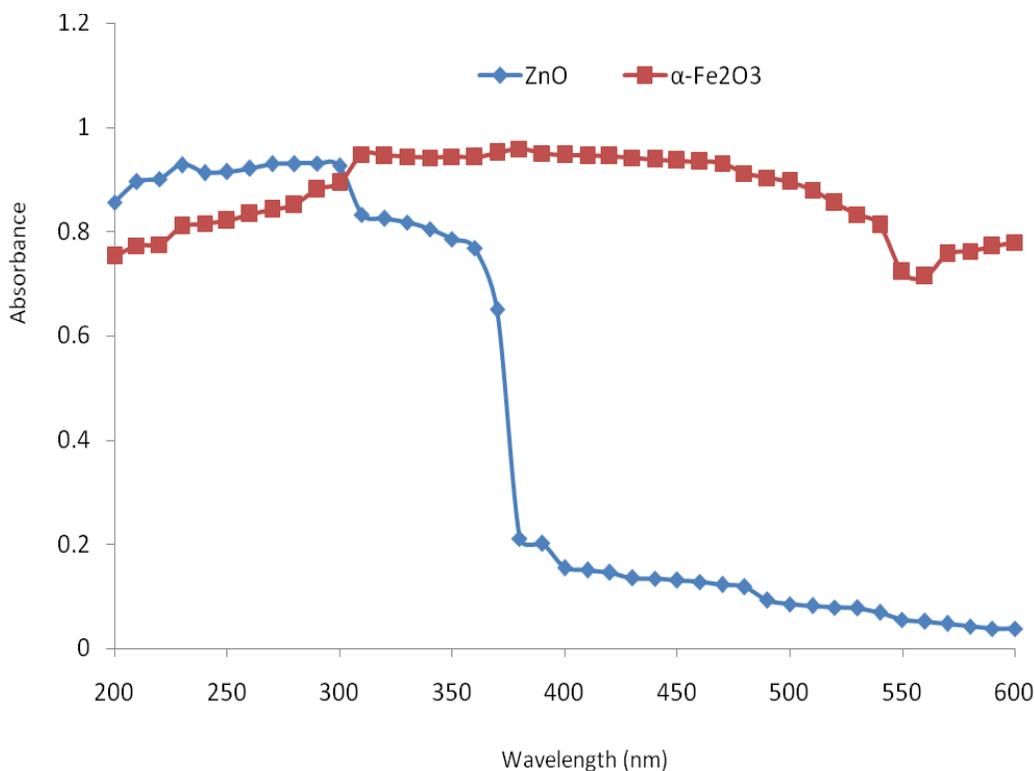


Figure 3. UV-Vis absorption spectra of the synthesized ZnO and $\alpha\text{-Fe}_2\text{O}_3$.

reached 52% and 86% for ZnO and $\alpha\text{-Fe}_2\text{O}_3$, respectively, within 6 h. This result indicates that the synthesized $\alpha\text{-Fe}_2\text{O}_3$ has a better photocatalytic activity for the degradation of phenol than ZnO.

The pseudo first order kinetics equation (3) is often used to describe the kinetics of photocatalytic processes (Hamza et al., 2011).

$$-\ln \frac{C_0}{C} = k_{app}t \quad (3)$$

Where k_{app} and t are the apparent rate constant of photocatalytic reactions and the irradiation time, respectively. The apparent rate constant is often chosen as the basic kinetic parameter for comparing different photocatalysts because it enables the determination of photocatalytic activity independent of the previous adsorption period in the dark and the concentration of solute remaining in the solution (Hamza et al., 2011). As seen in Figure 5, a linear relationship (with $R^2 > 0.90$) exists between $-\ln(C_0/C)$ and irradiation times, t , for both ZnO and $\alpha\text{-Fe}_2\text{O}_3$. Hence, the photocatalytic degradation of phenol on both ZnO and $\alpha\text{-Fe}_2\text{O}_3$ follows pseudo-first order kinetics. The apparent rate constants (k_{app}) were found to be 0.139 hr^{-1} and 0.310 hr^{-1} for ZnO and $\alpha\text{-Fe}_2\text{O}_3$, respectively.

The higher photocatalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ can be attributed to the low band gap of $\alpha\text{-Fe}_2\text{O}_3$. The band gap

$\alpha\text{-Fe}_2\text{O}_3$ is 2.1 eV (590 nm) which falls in the visible light region of the electromagnetic spectrum (400 - 800 nm). Visible light constitutes about 46% of the solar spectrum (Casbeer et al., 2012). Hence, $\alpha\text{-Fe}_2\text{O}_3$ is a good absorber of solar light and utilizes the absorbed solar light photons to drive photochemical reactions under visible light irradiation better than ZnO. The band gap ZnO is 3.2 eV which falls in the ultra violet light region of the electromagnetic spectrum (200 -400 nm). This makes ZnO less active photocatalyst under solar irradiation. It should be noted Valenzuela et al. (2002) found ZnO to be more active than $\alpha\text{-Fe}_2\text{O}_3$ under ultraviolet illumination (Valenzuela et al., 2002). Ultraviolet light constitutes about 5% of the solar spectrum (Casbeer et al., 2012). The larger specific surface area of $\alpha\text{-Fe}_2\text{O}_3$ ($162.3 \text{ m}^2/\text{g}$) may also be responsible for the observed higher photocatalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ when compared with ZnO ($39.5 \text{ m}^2/\text{g}$). Generally, the efficiency of heterogeneous catalytic processes increases with increase in the specific surface area of the catalyst.

Conclusions

ZnO and $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were synthesized and characterized using XRD, UV/Vis and modified BET techniques. $\alpha\text{-Fe}_2\text{O}_3$ was found to exhibit better photocatalytic activity than ZnO under solar light irradiation due to the narrower band gap and larger

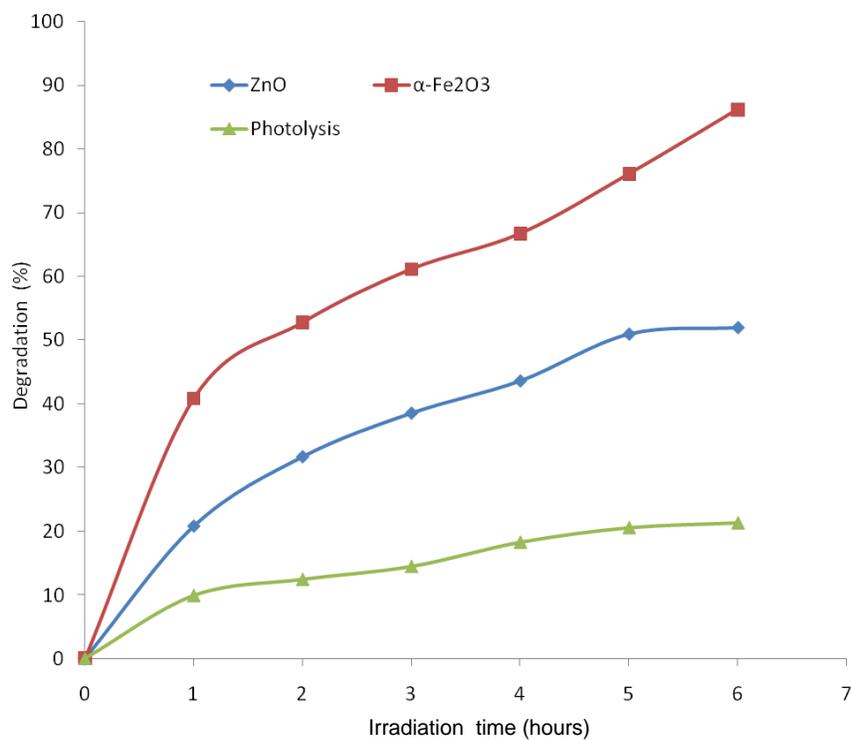


Figure 4. Effect of irradiation time on the photolytic and photocatalytic degradation of phenol using ZnO and α -Fe₂O₃.

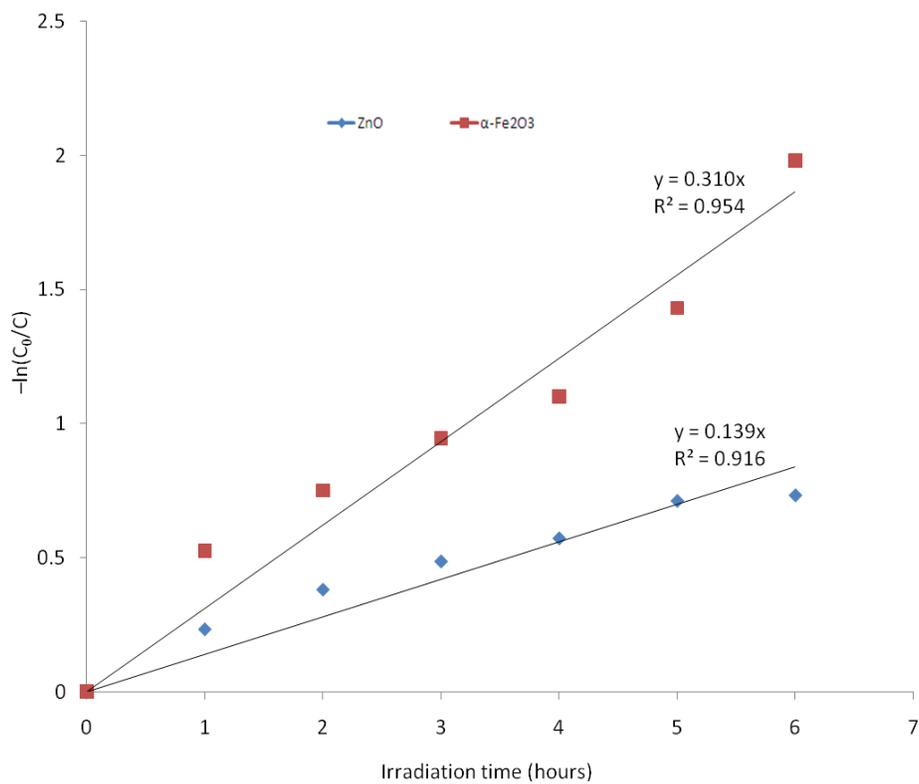


Figure 5. Pseudo first order kinetic plot for the photocatalytic degradation of phenol using ZnO and α -Fe₂O₃.

specific surface area of $\alpha\text{-Fe}_2\text{O}_3$ when compared with ZnO. The photocatalytic degradation of phenol follows pseudo-first order kinetics on both ZnO and $\alpha\text{-Fe}_2\text{O}_3$.

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