

Tổng hợp CeO_2 và ứng dụng xử lý chất màu hữu cơ trong môi trường nước

TÓM TẮT

Nghiên cứu này tổng hợp vật liệu CeO_2 sử dụng hai tác nhân tạo gel là axit tataric và PVA bằng phương pháp đốt cháy. Các đặc trưng được sử dụng để phân tích mẫu tổng hợp được là DTA-TGA, XRD, BET, SEM. Vật liệu tổng hợp ở các điều kiện tối ưu được ứng dụng xử lý xanh methylene (MB) trong môi trường nước. Kết quả phân tích MB cho thấy hiệu suất xử lý đạt gần 80 % ở pH4, nồng độ đầu vào của chất ô nhiễm 10 ppm, hàm lượng chất xúc tác 1 g/L.

Từ khóa: CeO_2 , PVA, axit tataric, xanh methylene

Synthesis of CeO₂ and its application for treating organic dyes in water

ABSTRACT

The CeO₂ material was synthesized using two gelling agents: tartaric acid (A) and PVA (P) through the combustion method. DTA-TGA, XRD, BET, and SEM methods were employed to analyze the characteristics of the synthesized material. The synthesized materials, prepared under optimal conditions, were utilized for the treatment of methylene blue (MB) in water. The efficiency achieved nearly 80% at pH 4 with an input concentration of the pollutant at 10 ppm and a catalyst concentration of 1 g/L.

Keywords: CeO₂, PVA, tartaric acid, methylene blue.

1. INTRODUCTION

Currently, environmental pollution poses a significant global challenge, including in Vietnam. Untreated or improperly treated waste released into the environment pollutes the soil, water, and air, directly impacting human life. Various methods are being applied and researched to treat pollutants, each with its own set of advantages and disadvantages.

Recently, photocatalytic method using CeO₂ catalyst has received research attention. Research results showed the effectiveness of CeO₂ in treating pollutants that are difficult to biodegrade^{1,2} as well as pigments^{3,4}. The advantages of CeO₂ are manifested in its structure. According to research⁵, in the unit structure of CeO₂, the cation Ce⁴⁺ was easily replaced by Ce³⁺. To compensate for the charge, the part of the oxygen elements were lost and created oxygen vacancies. Therefore, CeO₂ was converted to the form CeO_{2-n}. These oxygen vacancies were the reason for their effectiveness in catalytic reactions.

CeO₂ material was synthesized by many different methods such as hydrothermal⁶, sol-gel⁷, combustion method⁸...or a combination of methods. The combustion method offers the advantage of simplicity and the capability to synthesize a large quantity of material. In this study, two gelling agents, PVA and tartaric acid, were combined. The addition of tartaric acid to the reaction mixture enhanced its complexation ability, provided additional heat, reduced the concentration of PVA, and lowered the synthesis temperature of the material.

2. EXPERIMENT

2.1. Material synthesis process

Oxide nanoparticles of CeO₂ were synthesized by the combustion method. The gelling agents were dissolved in water with salt solutions of Fe³⁺ and Ce³⁺ in appropriate molar ratios. The solution was stirred and heated until transparent gel was formed. The formation gel had high viscosity and was dried for 2 hours at 110 °C. Finally, it formed a puffy, spongy mass. Material products were obtained after calcinating at different temperatures. pH buffers were used to investigate desire pH. The chemicals used in this study were analytical quality.

2.2. Photocatalytic process

Solutions containing defined concentrations of contaminants and catalyst were added to the reactor system (250 mL). The cup was covered with aluminum foil. The solution was stirred using a magnetic stirrer until adsorption equilibrium was reached. Afterthat, the mixture was lit by LED light with power 220V, 30W with different times. Methylene blue (MB) concentration was analyzed using a UV-Vis spectrophotometer (CE-2011).

3. RESULTS AND DISCUSSION

3.1. Effect of calcination temperature

Different thermal analysis method was used to investigate calcination temperature of dried sample synthesized gelation temperature of 80 °C; pH4; Ce/AP ratio = 1/3; AP ratio = 1/1. The results were shown in figure 1.

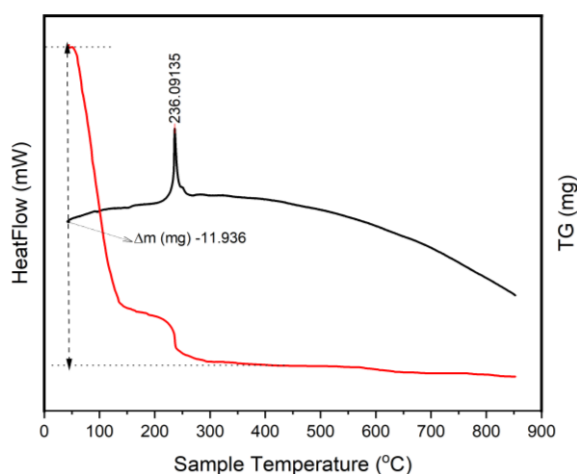


Figure 1. DTA – TGA of gel sample

Figure 1 depicts a rapid weight loss observed within the temperature range of 30 to 300 °C, attributed to both dehydration and decomposition of PVA and tartaric acid within the sample. This phenomenon aligns with the distinct exothermic peak recorded at 236.09 °C on the DTA curve. Subsequently, minimal mass variation was noted above the TGA curve, indicative of the formation of the pure product.

To examine the formation of CeO₂ material, the sample underwent calcination at various temperatures. The outcomes are illustrated in Figure 2

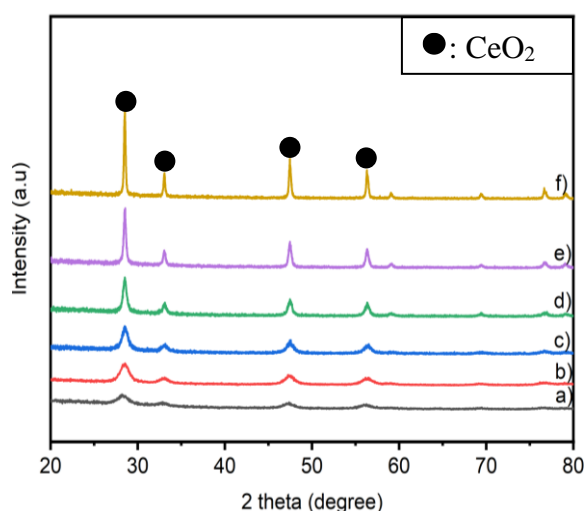


Figure 2. XRD diagrams of samples at different temperatures a)300 °C; b)400 °C; c)450 °C; d)500 °C; e)600 °C; f)700 °C

Characteristic peaks of CeO₂ began to appear at low temperatures of 300 °C, and the peaks formed more clearly when sample was calcined at higher temperatures. Here the calcination temperature of 400 °C was chosen for further studies.

3.2. Effect of pH

After choosing the appropriate calcination temperature, the sample was surveyed to select the optimal pH for the synthesis process. Sample was kept at conditions: gelation temperature 80 °C; Ce/AP ratio = 1/3; AP ratio = 1/1; calcinating temperature 400°C and pH values were changed by pH2, pH3, pH4. The results were shown in figure 3.

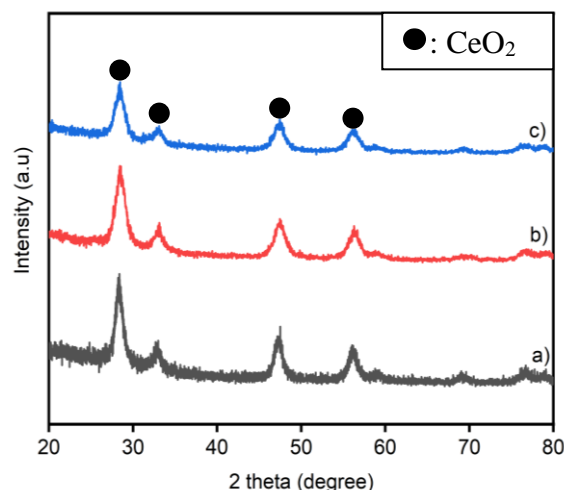


Figure 3. XRD diagrams of samples at a)pH2; b)pH3; c)pH4

Figure 3 distinctly displays the formation of characteristic peaks specific to CeO₂. The findings indicate that pH did not significantly influence the phase formation process of CeO₂ oxide in this study. However, at pH 4, the characteristic peak at $2\theta = 26^\circ$ exhibited a broader width compared to other values. This suggests the potential formation of smaller-sized oxide particles. Consequently, pH 4 was chosen for further research.

3.3. Effect of Ce/AP ratio

The ratio of metal and the gelling agent mixture were studied. The sample was synthesized at a gelation temperature of 80°C; AP ratio = 1/1; calcinating temperature 400°C; pH4; and Ce/AP ratios were changed at values of 9/1; 3/1; 1/1; 1/3; 1/9. Figure 4 showed the results of XRD diagrams of the synthesized samples.

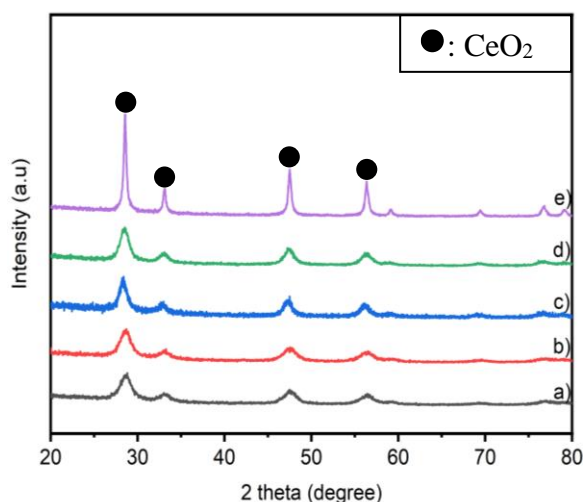


Figure 4. XRD diagrams of samples with different Ce/AP ratios a) Ce/AP = 9/1; b) Ce/AP = 3/1; c) Ce/AP = 1/1; d) Ce/AP = 1/3; e) Ce/AP = 1/9

The results in figure 4 were shown that ratios of Ce/AP = 9/1; Ce/AP = 3/1; Ce/AP = 1/1 of the amount of agent used to form complexes with metal ions were not enough. Therefore, the characteristic peaks of CeO₂ formed were not clear and unstable. At ratios of Ce/AP = 1/3; Ce/AP = 1/9, characteristic peaks were clearly shown. The ratio of Ce/AP = 1/3 was chosen for further studies.

3.4. Effect of gel formation temperature

To investigate gel formation temperature, the sample was synthesized at conditions Ce/AP ratio = 1/3; AP ratio = 1/1; calcinating temperature 400 °C; pH4, and gel formation temperatures were changed at 40 °C, 60 °C, 80 °C, 100 °C. The results were shown in Figure 5.

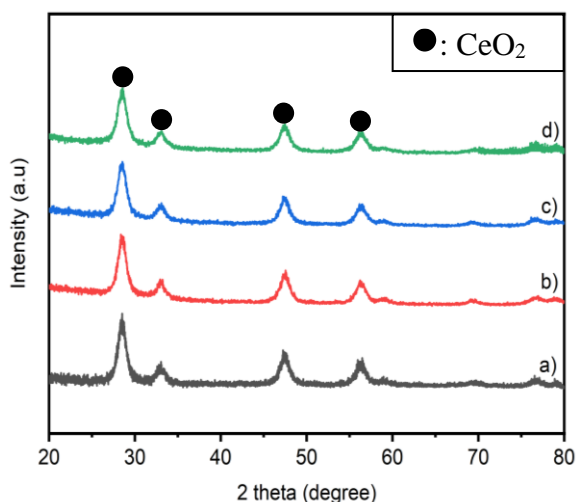


Figure 5. XRD diagrams of sample at different gel formation temperatures a) 40 °C, b) 60 °C, c) 80 °C, d) 100 °C

The synthesis time for sample preparation was observed to be prolonged, taking 8 hours at 40 °C and 4 hours at 60 °C. Surprisingly, at 100 °C, although the synthesis duration was shorter (an hour), the characteristic peaks of CeO₂ were distinctly evident in the XRD pattern. However, significant noise in the background suggested potential instability in the product. Conversely, at 80 °C, the synthesis duration of 2 hours was sufficient for uniform distribution of metal ions within the complexing agent's network, resulting in clear and well-defined peaks of CeO₂ in the XRD pattern. Consequently, a temperature of 80 °C was selected for synthesizing the desired sample

3.5. Material characteristic after choosing optimum conditions

The CeO₂ oxide successfully synthesized under the studied conditions was employed for decomposing pollutants via a photocatalytic process. This process was notably influenced by factors such as grain size, material surface area, and more. The material characterization results are presented in Figure 6 and Table 1.

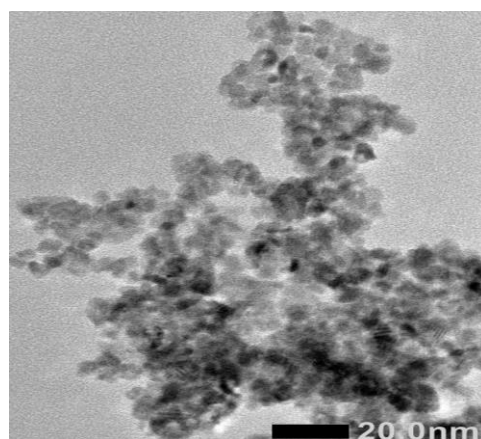


Figure 6. TEM image of CeO₂

Figure 6 showed that the oxide nanoparticles of CeO₂ were spherical with an average size of about 10 nm. When compared with similar studies^{9,10} that used only alone gelling agent the results were shown in Table 1.

Table 1. Comparison of CeO₂ material formed by using gel agents PVA, AT and mixture of PVA and AT

Gel agent	Calcination temperature (°C)	BET (m ² /g)
PVA	180	35.0
AT	600	38.57
AP	400	72.97

The calcination temperature of the sample using the AP gelling agent mixture was lower by 200 °C compared to the sample using AT alone. Additionally, the specific surface area of the sample using the AP gelling agent mixture was nearly double that of the sample using the gelling agent alone. This demonstrates the advantage of employing a mixture of gelling agents, PVA and AT. The combination enhanced the ability to form complexes with AT and achieve even distribution on the structural net of PVA. The even distribution of heat reduced the required heating temperature, resulting in a final product with a larger specific surface area, thereby creating favorable conditions for the decomposition of pollutants.

3.6. Photocatalytic process to decompose organic pigment of CeO₂ material

3.6.1. Effect of catalyst concentration

The material was continued to research on the influence of catalyst content on the MB decomposition process. The initial concentration of the pollutant was 10 ppm, pH 4, the catalyst content was changed at values of 0.25 g/L, 0.5 g/L, 1 g/L, 1.5 g/L. The results were shown in figure 7.

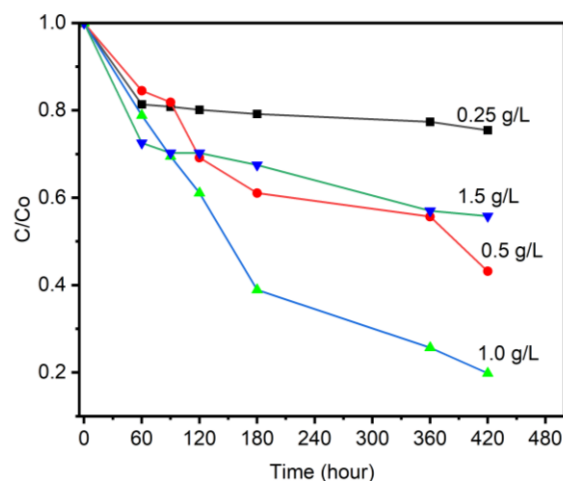


Figure 7. Effect of catalyst content to MB decomposition over time

The results demonstrated that as the catalyst content increased, the efficiency of MB treatment also increased over time, reaching its peak at a catalyst content of 1.0 g/L after 7 hours of treatment (80%). However, with a further increase in the catalyst content to 1.5 g/L, the efficiency of MB treatment decreased. This could be attributed to the material's black color, which potentially reduced the amount of light reaching

the material, thereby affecting the efficiency of the pollutant treatment process.

3.6.2. Effect of initial concentration

The initial pollutant concentration was changed at 5 ppm, 10 ppm, 15 ppm at pH4, catalyst content 1 g/L. The results were shown in figure 8.

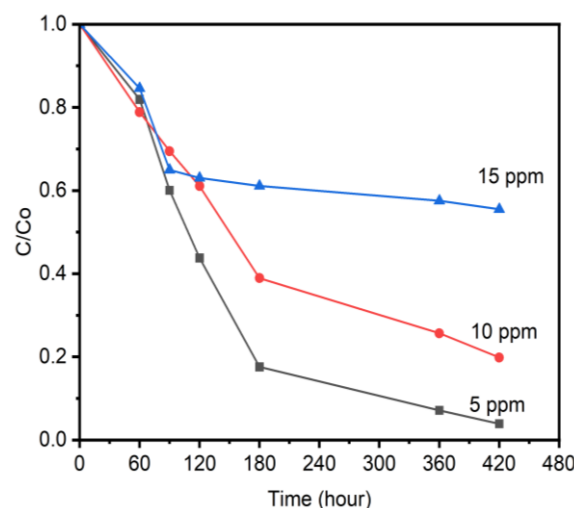


Figure 8. Effect of initial concentration to MB decomposition over time

The initial concentration of the pollutant greatly affected the pollutant treatment process. MB concentration was increased therefore it led to an increase in the amount of pollutants in the reaction mixture. With the same catalytic content and a certain number of active sites, the amount of MB adsorbed on these active sites were greater. Therefore, the number of active sites were not enough to decompose this amount of pollutant. The efficiency of decomposing pollutants decreased.

4. CONCLUSION

Oxide nanoparticles of CeO₂ were successfully synthesized under optimized conditions: calcination temperature at 400 °C, pH at 4, Ce/AP ratio of 1/3, AP ratio of 1/1, and gelation temperature at 80 °C. The resulting nanoparticles exhibited a spherical shape with an average particle size of approximately 10 nm and a surface area of 72.97 m²/g, nearly doubling that achieved when using either the gelling agent PVA (35 m²/g) or AT (38.57 m²/g) individually.

The photocatalytic process utilizing these CeO₂ nanoparticles demonstrated an efficiency of 80% in treating MB under conditions of pH 4, initial MB concentration of 10 ppm, catalyst content at 1 g/L, and a reaction duration of 7 hours.

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