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

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TÓM TẮT

Nghiên cứu này tổng hợp vật liệu CeO_2 sử dụng hai tác nhân tạo gel là tartaric acid (A) và polyvinyl alcohol (P) 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 lí methylene blue (MB) trong môi trường nước. Kết quả phân tích MB cho thấy hiệu suất xử lí 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, tartaric acid, MB.*

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Synthesis of CeO_2 and its application for treating organic dyes in water

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ABSTRACT

The CeO_2 material was synthesized using two gelling agents: tartaric acid (A) and polyvinyl alcohol (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 pH4 with an input concentration of the pollutant at 10 ppm and a catalyst concentration of 1 g/L.

Keywords: *CeO_2, 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 CeO_2 catalyst has received research attention. Research results showed the effectiveness of CeO_2 in treating pollutants that are difficult to biodegrade[1,2] as well as pigments.[3,4] The advantages of CeO_2 are manifested in its structure. According to research,[5] in the unit structure of CeO_2, the cation Ce^{4+} was easily replaced by Ce^{3+}. To compensate for the charge, the part of the oxygen elements were lost and created oxygen vacancies. Therefore, CeO_2 was converted to the form CeO_{2-n}. These oxygen vacancies were the reason for their effectiveness in catalytic reactions.

CeO_2 material was synthesized by many different methods such as hydrothermal,[6] sol-gel,[7] combustion method[8]...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.

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2. EXPERIMENT

2.1. Material synthesis process

Oxide nanoparticles of CeO_2 were synthesized by the combustion method. The gelling agents were dissolved in water with salt solutions of Ce^{3+} 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 ^oC. 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

Research investigated the degradation of MB via photocatalytic processes employing CeO_2 nanoparticle oxides. Initially, a solution containing a specified concentration of the contaminant and catalyst was introduced into the reactor system (250 mL). Following this, the suspension was stirred in darkness for 60 minutes to establish an adsorption/desorption equilibrium before irradiation. After that, the mixture was lit by LED light with power 220 V, 30 W with different times. At specific time points, approximately 5 mL of the mixture was withdrawn, centrifuged, and subsequently filtered to remove the residual catalyst particulates for analysis. The concentration of MB was determined using UV-Vis spectroscopy (CE-2011) at a wavelength of 663 nm.

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 ^0C; pH4; Ce/AP ratio = 1/3; AP ratio = 1/1. The results were shown in Figure 1.

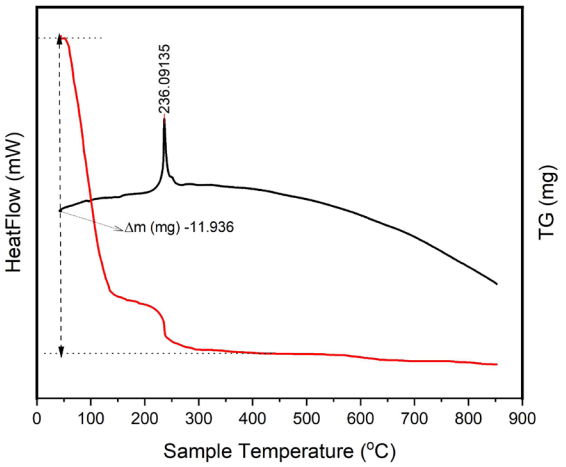

Figure 1. DTA – TGA of gel sample.

Figure 1 depicts a rapid weight loss observed within the temperature range of 30 to 300 ^0C, 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 ^0C 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 CeO_2 material, the sample underwent calcination at various temperatures. The outcomes are illustrated in Figure 2.

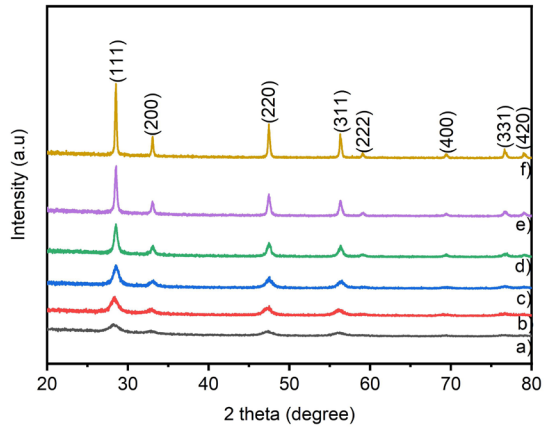

Figure 2. XRD diagrams of samples at different temperatures a) 300 ^0C; b) 400 ^0C; c) 450 ^0C; d) 500 ^0C; e) 600 ^0C; f) 700 ^0C.

The peaks located at 2θ = 28.99; 33.39; 47.91; 56.75; 59.1; 69.6; 76.5 and 79.47 correspond to the (111), (200), (220), (311),

(222), (400), (331), and (420) crystal planes of CeO_2, respectively, according to JCPDS card: 34-0394.[9] These peaks began to appear at low temperatures of 300 ^{0}C, and the peaks formed more clearly when sample was calcined at higher temperatures. Here the calcination temperature of 400 ^{0}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 ^{0}C; Ce/AP ratio = 1/3; AP ratio = 1/1; calcinating temperature 400 ^{0}C and pH values were changed by pH2, pH3, pH4. The results were shown in Figure 3.

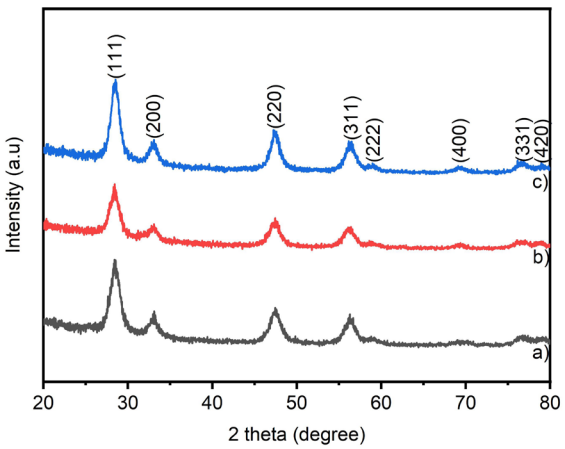

Figure 3. XRD diagrams of samples at a) pH2; b) pH3; c) pH4.

Figure 3 distinctly displays the formation of diffraction peaks specific to CeO_2. The findings indicate that pH did not significantly influence the phase formation process of CeO_2 oxide in this study. However, if the pH is low (pH2, pH3), it can break the polymer chains of PVA, reducing the uniform dispersion of metal cations in the network. The appropriate pH here is pH3, pH4. In the next study, pH4 was chosen.

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 ^{0}C; AP ratio = 1/1; calcinating temperature 400 ^{0}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.

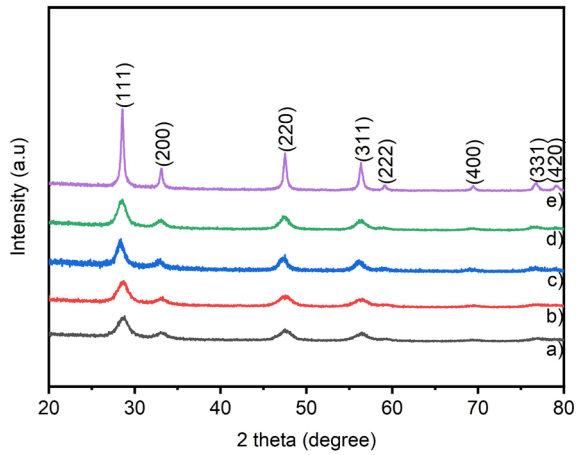

Figure 4. XRD diagrams of samples with different Ce/AP ratios a) Ce/AP = 9/1; b) Ce/AP = 3/1; c) Ce/AP = 1/1; d) Ce/AP =1/3; e) Ce/AP = 1/9.

At 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, resulting gels exhibited poor viscosity. When forming gels at Ce/AP = 1/3 and 1/9, it ensured the appropriate amount of gel-forming agent, leading to high viscosity gels. Upon thermal treatment, the products showed increased porosity and more uniform particle sizes. However, as shown in Figure 4, at the Ce/AP = 1/9, the peaks formed were higher and sharper compared to the Ce/AP = 1/3. This may indicate an increase in the crystal size of the obtained material. Therefore, the 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 ^{0}C; pH4, and gel formation temperatures were changed at 40 ^{0}C, 60 ^{0}C, 80 ^{0}C, 100 ^{0}C. The results were shown in Figure 5.

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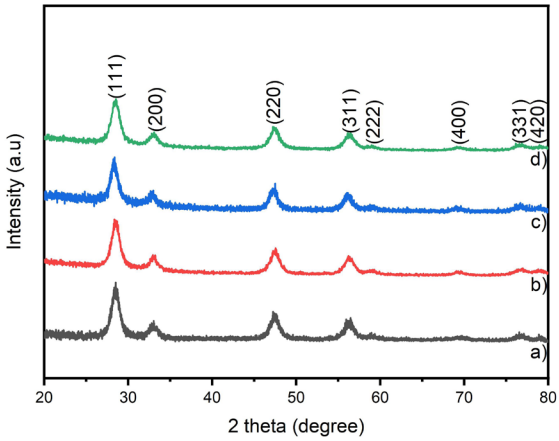

Figure 5. XRD diagrams of sample at different gel formation temperatures a) 40 ^{0}C, b) 60 ^{0}C, c) 80 ^{0}C, d) 100 ^{0}C.

The synthesis time for sample preparation was observed to be prolonged, taking 8 hours at 40 ^{0}C and 4 hours at 60 ^{0}C. Surprisingly, at 100 ^{0}C, although the synthesis duration was shorter (an hour), the characteristic peaks of CeO_2 were distinctly evident in the XRD pattern. However, significant noise in the background suggested potential instability in the product. Conversely, at 80 ^{0}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 CeO_2 in the XRD pattern. Consequently, a temperature of 80 ^{0}C was selected for synthesizing the desired sample.

3.5. Material characteristic after choosing optimum conditions

The CeO_2 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.

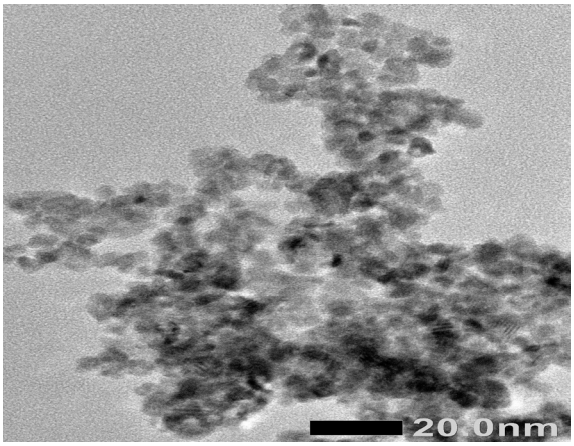

Figure 6. TEM image of CeO_2.

Figure 6 showed that the oxide nanoparticles of CeO_2 were spherical with an average size of about 10 nm. When compared with similar studies[10,11] that used only alone gelling agent the results were shown in Table 1.

Table 1. Comparision of CeO_2 material formed by using gel agents PVA, AT and mixture of PVA and AT.

Gel agent	Calcination temperature (^{0}C)	BET (m^2/g)	References
PVA	180	35.0	[10]
AT	600	38.57	[11]
AP	400	72.97	This study

The calcination temperature of the sample using the AP gelling agent mixture was lower by 200 ^{0}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. Figure 7 shows the N_2 adsorption–desorption isotherms and the pore size distribution plot of the CeO_2 samples.

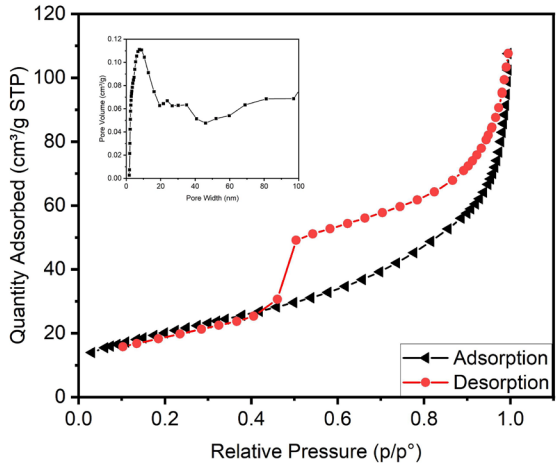

Figure 7. Nitrogen adsorption–desorption isotherm and the pore size distribution plot for the synthesized CeO_2 sample.

Figure 7 shows that the adsorption and desorption isotherms of the CeO_2 material samples exhibit type IV (according to the IUPAC classification), characteristic of mesoporous structures. The average pore diameter was calculated using the BJH method to be 9.7 nm.

3.6. Photocatalytic process to decompose organic pigment of CeO_2 material

3.6.1. Effect off 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 8.

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.

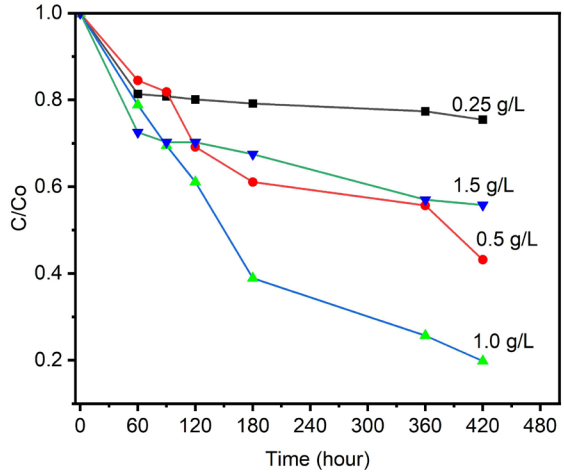

Figure 8. Effect of catalyst content to MB decomposistion over time.

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 9.

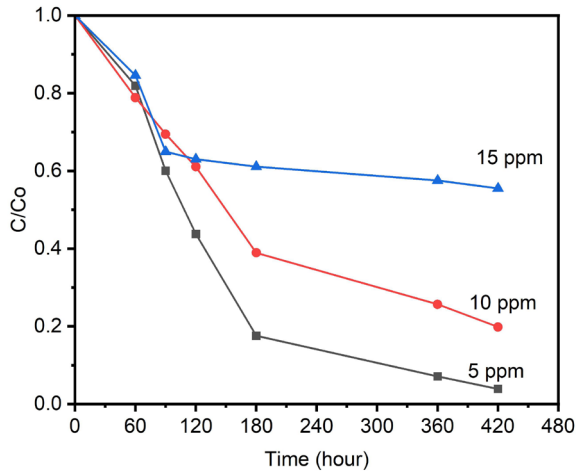

Figure 9. Effect of initial concentration to MB decomposition over time.

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.

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During photocatalysis, electron/hole pairs are formed under appropriate light conditions. Similar to the study by Le Thi Thanh Tuyen,[9] under UV light irradiation, these electrons further react with dissolved oxygen to generate superoxide radical anions ($O_2^{\bullet-}$), while h^+ in the valence band reacts with adsorbed water and produces more hydroxyl radicals (•OH). These strong oxidizing radicals are reactive species which are mainly responsible for degradation of MB.

4. CONCLUSION

Oxide nanoparticles of CeO_2 were successfully synthesized under optimized conditions: calcination temperature at 400 ^{0}C, pH4, Ce/AP = 1/3, AP = 1/1, and gelation temperature at 80 ^{0}C. The resulting nanoparticles exhibited a spherical shape with an average particle size of approximately 10 nm and a surface area of 72.97 m^2/g, nearly doubling that achieved when using either the gelling agent PVA (35 m^2/g) or AT (38.57 m^2/g) individually.

The photocatalytic process utilizing these CeO_2 nanoparticles demonstrated an efficiency of 80 % in treating MB under conditions of pH4, initial MB concentration of 10 ppm, catalyst content at 1 g/L, and a reaction duration of 7 hours.

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