Study the Catalytic Activity of CeO\(_2\) Catalyst for the Oxidative Degradation of Orange G Dye in Aqueous Solution

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Abstract

The oxidative degradation of Orange G dye by nanosized CeO\(_2\) catalyst has been performed in this study. The catalyst was prepared by precipitation method. Various characterization techniques were carried out to study the physical and chemical properties of the synthesized catalyst. The XRD result confirms well the formation of CeO\(_2\) cubic phase. The FTIR result showed the effect of calcination temperature for CeO\(_2\) was clearly observed due to reduction in band intensity compared to uncalcined Ce nitrate sample. Meanwhile, the diffused reflection spectra recorded reflection spectra at 414 nm with an energy gap of 3.2 eV. The decolorization of Orange G dye by oxidation process were carried out under various conditions such as, the effects of H\(_2\)O\(_2\) dosage, pH, catalyst dosage and the temperature of reaction. The optimum conditions for the highest decolorization efficiency (100%) were achieved at 10 mg/L of orange G dye with catalyst dosage of 1.5 g/L, pH 2, reaction temperature of 65 °C and 0.1 mL H\(_2\)O\(_2\).

Keywords: Cerium oxide, Oxidation process, Nanoparticles, Heterogeneous catalyst.

1. Introduction

Different shapes and sizes of semiconductor nanoparticles have been synthesized to be used in the application of advanced oxidation process [1]. Generally, as the particles size reduces to nanostructure-scale then, the properties of material will dramatically changes leading to recent advances in synthesis of nanostructures. The particle size of materials affects their basic properties such as lattice symmetry, cell parameters, and structural characteristics [2].

The nano structure of metal oxides can show unique chemical properties due to their limited size and high density of corner or edge surface sites. Among different metal oxides, special attention has been focused on the formation and properties of cerium oxide which is important as heterogeneous catalyst [3]. Cerium oxide that has a wide band gap is consider a good semiconducting material which is familiar for its catalytic properties. Cerium, one of lanthanide series exhibit both oxidation states \(^{"3}\) and \(^{"4}\) and has high ability for oxidation/reduction reactions very easily. Because of this excellent property cerium oxide is used in various applications such as catalytic converters, solid oxide fuel cells and oxygen buffers [4].

Up to now various method have been developed for the synthesized of cerium oxide nanostructure, such as chemical vapor deposition, electrochemistry, templates, photoinduced conversion, biological synthesis. Different nanoparticles sizes of CeO\(_2\) have been synthesized with different preparation method leading to produce different chemical, physical and optical properties of CeO\(_2\). The precipitation method has attracted the most attentions owing to the advantages of simple process, easy scale-up and low cost [5].

Cerium dioxide has been taken a great interest in the application of heterogeneous photocatalytic reactions. This was due to the properties of CeO\(_2\) as a semiconducting material that absorbs light in the near UV and also slightly in the visible region. However, there was no report for the use of cerium oxide as catalyst for the degradation of organics dyes using oxidation process. As such,
this report have been focused on the degradation of orange G dyes using nano CeO₂ as heterogeneous catalyst using oxidation process. Different characterization techniques were conducted including characterization technique using X-ray diffraction, FTIR, diffuse reflectance spectra and AFM technique. Efforts have been made to investigate the effects of adding H₂O₂, solution acidity and the amount of catalyst dosage. In this study, the stability of the catalyst is excluded as the aim was focusing on the experimental work covering thorough characterization and process study under various conditions.

2. Materials and Methods

The pure metal cerium nitrate purchased from BDH. Meanwhile, hydrogen peroxide (30% analytical grade) was supplied from Analar. The sodium carbonate as a precipitating agent was purchased from Merck. The pollutant model of Orange G dye was obtained from Fluka and its properties are listed in Table 1.

Table 1. The structure and properties of Orange G dye.

<table>
<thead>
<tr>
<th>Molecular structure</th>
<th>Other names</th>
<th>Molecular weight</th>
<th>Color</th>
<th>λmax</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid Orange 10</td>
<td>452.38 g/mol</td>
<td>16230</td>
<td>478 nm</td>
</tr>
</tbody>
</table>

Preparation Method

Pure ceria oxide has been prepared by precipitation method technique according to the method similar to Pradhan and Parida, (2010). The sodium carbonate was used as a precipitating agent at room temperature. The concentration of the prepared sample for pure catalyst was fixed at 0.1 M.

A known volume of pure oxide was taken and Na₂CO₃ of 0.25 M was added into the solution until the pH reached to 9. At that pH, a white precipitate solid was formed then the products were collected by filtration, washed several times with distilled water, and dried at 110 °C. Finally, the prepared catalyst was denoted as CeO₂ after its calcination at 500 °C for 4 h.

3. Characterization Techniques

The characterization of the catalyst with different analytical techniques was performed on the catalyst. X-ray diffraction (XRD) was used to study the crystalline phase of cerium oxide nanoparticles. The FTIR spectroscopic analysis was carried out using Bruker Alpha spectrophotometer. Meanwhile, the reflection spectra of the solid samples were measured using the diffraction spectrophotometer by (Perkin Elmer) with a wavelength range between 190 and 1,300 nm. The particle size analyzer was carried out by Brookhaven instrument. The roughness of the catalyst surface was checked using AFM technique.

Reaction Procedure and Analytical Method

The experimental runs were carried out in a 250 mL conical flask as a reactor equipped with a magnetic stirrer and heater. Water containing orange G dye (10 mg/l) was transferred to the glass reactor. Thereafter, the catalyst was added to the solution. The temperature of the reaction mixture was controlled using heater to the desired value. Hydrogen peroxide was added, the runs were conducted at 60 °C and the samples were taken at periodic intervals i.e. (10 min). The maximum absorbance wavelength of Orange G dye was carried out using spectrophotometric analysis to determine the maximum absorption of the dye which was fixed at 478 nm. Beer-Lambert law was used to calculate the concentration of the liquid samples based on measuring the absorbance of each sample at its maximum absorbance wavelength. After a certain period of catalytic reaction, a liquid sample was withdrawn and centrifuged at 3000 rpm to separate the solid catalyst from liquid sample. The catalytic activity represented by the color removal was calculated based on equation (1) [7]:

\[ \text{Decolorization Efficiency} \% = \left[ \frac{C_o - C_t}{C_o} \right] \times 100 \]

\[ \text{...(1)} \]

where, \(C_o\) is concentration of dye in (mg/L), \(C_t\) is the concentration of dye in (mg/L) at different reaction time and \(t\) (min).
4. Result and Discussion

4.1. X-ray Diffraction

Fig. 1 shows the indexed XRD pattern for the prepared CeO$_2$ sample. The CeO$_2$ show high crystalline structure of peaks that confirms the formation of cubic phase CeO$_2$ samples. The d-spacing values of the cerium oxide sample matches well the standard code of 96-900-9009. The characteristic reflection at 2θ values were at 28.78°, 33.27°, 47.67°, 56.48°, 59.19°, 69.53° and 76.82° respectively. This result was in agreement with Chelliah et al., (2012) and Teo et al., (2014). As the Xrd result confirms the formation of cerium oxide phase this indeed improve the success of preparation method.

![Fig. 1. X-ray diffraction of CeO$_2$](image)

4.2. Fourier Transformed Infrared Spectroscopy (FTIR) Analysis

The FT-IR spectrum of the CeO$_2$ annealed at 500 °C is shown in Fig. 2. Fig. 2 (a), shows the broad absorption band located around 3429 cm$^{-1}$ corresponds to the O-H stretching vibration of residual water and hydroxyl groups, while the absorption band at 1647cm$^{-1}$ can be attributed to the O-H vibration in absorbed water on the sample surface. Similar results were detected with Kumara et al., (2013). The effect of calcination temperature for CeO$_2$ was clearly observed due to the reduction of those band intensity compared to uncalcined Ce nitrate sample in Fig 2 (b). Channiel et al., (2014) reported that the energy gap of CeO$_2$ nanoparticles was 3 ev. Khan et al., (2013) reported that the energy gap of CeO$_2$ nanoparticles was about 4.16 ev. Meanwhile Chaiwichian et al., (2012) reported that the energy gap of CeO$_2$ nanoparticles was 2.77 ev with particle size of 5-10 nm. The optical properties of the solid catalyst affected directly by the preparation method thus affect its energy band gap.

![Fig. 2. Fourier transformed infrared spectroscopy of (a) CeO$_2$ calcined at 500 °C (b) uncalcined cerium nitrate.](image)

4.3. UV-vis Diffuse Reflectance Spectra Analysis and Particle Size Analyzer

The diffuse reflectance spectra of CeO$_2$ nanoparticles were recorded in Fig. 3 (a) using a UV-Vis diffuse reflectance spectra over the wavelength from 200-1200 nm. The cerium oxide nanoparticles shows a reflection spectra at 414 nm. The optical band gap energy of the prepared sample was detected in the sudden fall region at a certain wavelength. The band gap energy value was determined from the extrapolation of the straight line for the graph figured between the $[\ln [(R_{max}-R_{min})/(R-R_{min})]]^2$ versus photon energy $(h\nu)$ (as abscissa) kumar et al. (1999) as in Fig. 3 (b). Channei1 et al., (2014) reported that the energy gap of CeO$_2$ nanoparticles was 3 ev. Khan et al., (2013) reported that the energy gap of CeO$_2$ nanoparticles was about 4.16 ev. Meanwhile Chaiwichian et al., (2012) reported that the energy gap of CeO$_2$ nanoparticles was 2.77 ev with particle size of 5-10 nm. The optical properties of the solid catalyst affected directly by the preparation method thus affect its energy band gap.

Fig.3 (c) presents the particles size of CeO$_2$ catalyst that was analyzed by the particle size analyzer. The result shows that the particle size of CeO$_2$ was about 2.03 e$^{+3}$ nm. According to literature, different reports have been reported the particle size of cerium oxide with different values depending on various types’ techniques such as SEM, TEM or particle size analyzer. Several factors can effects on particle size of the materials such as the preparation methods, calcination temperatures and raw materials used during the preparation methods etc....
4.4. Atomic Force Microscopy (AFM)

Fig. 4 shows the AFM 3D image of CeO$_2$ catalyst calcined at 500 °C. The image detects a separated conical nano columnar structure with measured roughness of (Area Ra 0.825 nm) and (Area RMS 1.03 nm). The measured roughness reported earlier for pure CeO$_2$ thin film by Durrani et al. (2008) with (Area Ra 2.38) and (Area RMS 3.11).

4.5. The Optimum Reaction Condition for the Decolorization of Orange G dye

4.5.1. Effect of pH

The effect of pH on the catalytic activity of CeO$_2$ nanoparticles for the decolorization of orange G dyes with an initial dye concentration of 10 mg/L over a pH range of 2–10. The pH of the dye solution was adjusted by adding suitable amounts of 1M HCl and NaOH. The decolorization efficiency at different pH solutions is shown in Fig. 5. The results show that the maximum decolorization efficiency of 100% was obtained at a pH of 2 after 60 min of oxidation process. At pH 5 and 10, the decolorization of Orange G dye was almost the same range about 13%. This higher catalytic activity at pH 2 was referring to the higher OH radicals generated. Furthermore, as the orange G dye is an anionic dye, its adsorption mainly performed via an electrostatic interactions between the positive CeO$_2$ surface and orange G dye anions, leading to a maximum extent at pH 2. Bokare et al., (2008) also reported that higher catalytic activity for orange G dye i.e. 99% was achieved at pH 2 using bimetallic nanoparticles oxide of Fe-Ni catalyst. On other hand, the lower catalytic activity at higher pH values i.e. 5 and 10 could be referred to the self-decomposition reaction of H$_2$O$_2$ to H$_2$O and O$_2$.

4.5.2. Effect of Catalyst Dosage

The effect of catalyst dosage on the decolorization efficiency of orange G dye was investigated with different catalyst dosage ranging from 0.5 g/L up to 2 g/L with reaction condition of 10 mg/L concentration of dye, 0.1ml H$_2$O$_2$/100ml of reaction and solution acidity of 2.0 for 60 min of reaction time as in Fig. 6.
Before the starting of oxidation reaction, 30 min of mechanical stirring was observed until adsorption-desorption equilibrium was reached. The results showed that the adsorption rate was increased from 11% to 60% with an increase in catalyst dosage ranging from 0.5 g/L to 2 g/L, respectively. The presence of extra active sites and higher effective surface area enhance the adsorption rate in cerium oxide catalyst [17] as in Fig. 6.

With the start of oxidation reaction, the catalytic activity was increased from 14% to 100% for catalysts loading of 0.05 and 1 g/l respectively. However, as the catalyst dosage was further increase up to 2 g/l, insignificant difference in catalytic activity was notice after 60 min of oxidation reaction i.e. 100%. The synergistic effect between the heterogeneous catalyst/H2O2 system enhance the generation of radicals thus, improve the catalytic activity. Slavova et al., (2014) reported that higher catalyst loading in solution would result in higher dye removal efficiency. However, the variation in optimum values of the catalyst dosage based on the process environment, the structure of dye molecules and the catalyst properties.

4.5.3. Effect of Temperature

Reaction temperature is another important process parameter that has a significant effect on catalytic activity during the oxidation process. The effect of reaction temperature on the decolorization efficiency of orange G dye was detected throw a series of experiments within the catalyst loading used of 1.5 g/L, 10 mg/L initial concentration of dye, 0.1 ml H2O2/100 ml of reaction and pH of 2.0 by varying temperature from 25 °C to 65 °C as in Fig. 7. After 30 min of mechanical stirring between the nanoparticles of CeO2 and dye solution, the adsorption rate of Orange G dye was decreased as temperature increase. Mafra et al., (2013) reported that the fall in the adsorption capacity at elevated temperatures could be ascribed to the escape of the dye molecules from the catalyst surface and re-enters the liquid phase as an increase in temperature caused an increase in the speed of molecules. Consequently, as the oxidation reaction was started, the decolorization of orange G dye was significantly influenced by the reaction temperature and the decolorization was accelerated from 59% to 100% by a rise in temperature from 25 °C to 65 °C. This is because higher temperature increased the reaction rate between hydrogen peroxide and the catalyst, thus increasing the rate of generation of oxidizing species such as ‘OH radical.

4.5.4. Effect of H2O2 dosage

The catalytic activity based on color removal of Orange G dye was examined by changing the concentrations of hydrogen peroxide in the dye solution i.e. 0.05, 0.1 and 0.15 ml of H2O2/100 ml
of reaction volume within the catalyst loading used of 1.5 g/L, 10 mg/L initial concentration of dye, pH of 2.0 and reaction temperature of 65 °C as in Fig. 8. As the mechanical stirring was started, a certain amount of hydrogen peroxide was added into the reaction solution and the oxidation reaction was started. The H$_2$O$_2$ was consider as an external source and its addition into the reaction increase the possibility of radicals generation during the oxidation process. The optimum efficiency of 100% was found at 0.1 ml after 60 min of the reaction time as shown in Fig. 8. Above the optimum value, the decolorization efficiency of orange G dye was dropped to 50% at 0.15 ml H$_2$O$_2$. This reduction in catalytic activity as the amount of hydrogen peroxides increased was ascribed to its extra amount in the reaction that acts as scavengers to hydroxyl radicals [21].

5. Conclusion

The heterogeneous catalyst CeO$_2$ were successfully synthesized using precipitation method. Characterization results of XRD show high crystalline structure of peaks that confirms the formation of cubic phase CeO$_2$ samples. FTIR technique detected the effect of calcination temperature on the formation of CeO$_2$ due to the reduction of band intensity compared to uncalcined Ce nitrate sample. The UV-Vis diffuse reflectance spectrum for CeO$_2$ demonstrated the presence of optical band gap due to the sudden reduction in reflection spectra of the sample at 414 nm with an energy gap of 3.2 ev. Meanwhile the AFM 3D image of CeO$_2$ calcined at 500 °C reveals the formation of well separated conical nano columnar structure with measured roughness value of 1.03 nm. A process behavior of the catalyst was also successfully elucidated. The best conditions for the highest decolorization efficiency (100%) were achieved at 10 mg/L of orange G dye, catalyst loading of 1.5 g/L, pH 2, reaction temperature of 65 °C and 0.1 mL H$_2$O$_2$/100 mL solution. Hence, the prepared cerium oxide catalyst under oxidation reaction is a good environmental heterogeneous catalyst and can be widely used in the application of wastewater treatment method for organic dyes in effluents.

6. References

دراسة كفاءة السيريوم إوكسايد كعامل مساعد في تحسين صبغة الأورانج ج بواسطة عملية الأكدة

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الخلاصة

يهدف البحث دراسة عملية تحسين صبغة الأورانج ج بواسطة عملية الأكدة، ويوجد السيريوم إوكسايد النانوي بوصفة محظوظة والذي تم تصنيعه عن طريق عملية الترسيب، تم تشييده بنية الحفز المصنوع باستخدام عدة تقنيات ومنها، الشبكة الحيوية المائية، وتجرى القوة الذرية (XRD) وانسياب الخصائص (AFM)، وقياس فجوة الطاقة بطريقة FTIR الظاهرة الرابطة باستخدام UV، وتقوم بتوظيف تغير المعادلة الحرارية للفحص على ترددات XRD والانسياب الكيميائية للسيريوم إوكسايد والتي كانت فق مقاومة بالمادة الأولية، غير المعادلة (سيريوم نانية) أظهرت نتائج 3.2 ووجود جودة عند 414 nm وترددات 3.2 ev

بعد استكمال عملية التنشيط للعامل المساعد المصنوع تم دراسة العديد من متغيرات التفاعل التي لها تأثير مباشر على كفاءة ازالة اللون خلال وقت التفاعل ومنها: درجة الحموضة، كمية الهيدروجين بيروكسايد، كمية العامل المساعد، ودرجة الحرارة. وكانت أعلى كفاءة للعامل المساعد في وصلت الى 100% بدرجة حموضة 2، كمية العامل المساعد 1.5 غرام لكل 100 مل هيدروجين بيروكسايد/100 مل من حجم التفاعل مع تركيز ابتدائي للصبغة 10 المليو/لتر، ودرجة حرارة 25 درجة مئوية خلال 10 دقيقة من وقت التفاعل.