Sonocatalytic degradation of caffeine using CeO\textsubscript{2} catalyst: parametric and reusability studies

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Abstract. This work examined sonocatalytic degradation of caffeine in the presence of CeO\textsubscript{2} prepared by hydrothermal method. Several characterization techniques were used to study the CeO\textsubscript{2} including TEM, XRD and BET method. Effects of various parameters such as pH, initial concentration of caffeine and dosage of CeO\textsubscript{2} were investigated. This study also examined the reusability of CeO\textsubscript{2}. Results showed that the CeO\textsubscript{2} mixed shapes of crystallites consisting of rods and cubes with the specific surface area (S\textsubscript{BET}) and pore volume of 126.63 m\textsuperscript{2}/g and 0.4898 cm\textsuperscript{3}/g, respectively. About 95.5\% of caffeine degradation was achieved under the best parameter conditions i.e. at pH of 7.5, 5.0 mg/L of initial concentration of caffeine and 1.0 g/L of CeO\textsubscript{2} dosage within 150 min. It was also revealed that the operating parameters played major roles in caffeine degradation efficiency. In addition, the CeO\textsubscript{2} were quite stable since the efficiency of caffeine degradation achieved in the third cycle was 81.4\%.

1. Introduction
Caffeine is commonly employed as a stimulant in pharmaceutical and personal care products (PPCPs) [1] and as an ingredient in beverages such as coffee, tea, caffeinated soft drinks, chocolate and numerous food products [2]. Caffeine as one of the most frequently detected of PPCPs, has gained environmental concern due to its potential adverse effect on the aquatic organisms and environment [3]. Caffeine is recognized as a micropollutant and its presence in surface water, groundwater (from the wastewater treatment plants) [4] and drinking water [5] which can be detected at concentration level in the matter of a few μgL\textsuperscript{−1} or ngL\textsuperscript{−1} [6]. However, at high concentration, caffeine is known to be toxic [7].

Advanced oxidation processes (AOPs) have been recognized as an attractive technology to remove persistent organic pollutant from contaminated water. It involves the generation of reactive species mainly hydroxyl radicals (•OH) which could oxidize a broad range of organic pollutants that present in water. Sonocatalysis as one of AOPs potential process could treat caffeine or other organic micropollutants in wastewater [8–9]. This process utilizes ultrasonic irradiation in the presence of suitable semiconductor catalyst. The semiconductor materials that have been reported in previous studies are such as TiO\textsubscript{2} [9–10], ZnO [11], MnO\textsubscript{2} [12], FeCeO\textsubscript{3} [13] and many more. Among other catalysts, cerium oxide (CeO\textsubscript{2}) or ceria has received much attention recently due to its high temperature stability and non-toxic in catalytic applications [14]. Besides, CeO\textsubscript{2} or cerium-based materials have
gained increasing attention in photocatalysis application for the past decade as alternative of conventional photocatalyst, TiO$_2$ [14]. Therefore, this material is hardly studied for its sonocatalytic properties and only a few studies are available in the literature regarding the sonocatalytic activity of CeO$_2$ or ceria based [15–16].

In the present work, effects of various parameters such as pH, initial concentration of caffeine and catalyst dosage on the sonocatalytic degradation of caffeine under ultrasonic irradiation were studied to evaluate the performance of the catalyst. In addition, the reusability potential of catalyst was also demonstrated.

2. Materials and methods

2.1. Materials

Cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O) (99% purity) (Sigma-Aldrich), Sodium hydroxide (NaOH) (98% purity) (Merk) and hydrogen peroxide (H$_2$O$_2$) (30% purity) (Merk) were used as received without any purification. Caffeine powder (C$_8$H$_10$N$_4$O$_2$) with molecular weight of 194.19 g/mol was purchased from Merk and the structure of caffeine is shown in figure 1.

![Figure 1. Chemical Structure of Caffeine.](image)

2.2. Preparation of catalyst

Cerium oxide was prepared using a hydrothermal method according to the published procedure [17]. An amount of Ce(NO$_3$)$_3$·6H$_2$O was dissolved in 5 mL of deionized water. Then, 75 mL of NaOH solution (6.4 M) was added drop wise into the ceria precursor solution under vigorous stirring for 30 min. The above mixture was then transferred into a Teflon-lined stainless-steel autoclave and heated up to 100°C for 24 h. The resultant precipitant was then washed with two-litter deionized water and separated using centrifuge for three times. Then, the precipitate was dried in an oven at 60°C overnight.

2.3. Characterization of catalyst

X-ray powder diffraction (XRD) pattern of CeO$_2$ was recorded on an X-ray diffractometer (Bruker D8 Advance, Germany) using monochromatic Cu Kα as the radiation source ($\lambda = 1.5406$ Å), with an operating voltage of 40 kV and emission current of 40 mA. The diffractogram was measured from 10° to 70° (2θ) at step size of 0.020°. Then, the diffraction peaks of crystalline phases were compared with the standard compound in JCPDS data file. The morphology of CeO$_2$ was examined by transmission electron microscope (TEM) (ZEISS LIBRA 120 microscope) with an accelerating voltage of 100 kV. The textural properties of CeO$_2$ was estimated via adsorption-desorption of N$_2$ at -195.87°C using a Micromeritics instrument model ASAP 2020. The sample (0.1444 g) was degassed under vacuum at 250°C for four hours. The specific surface area was calculated using the standard Brunauer–Emmet–Teller (BET) method while the pore volume was calculated by Barret-Joyner-Halenda (BJH) method for mesopores analysis.
2.4. Experimental set-up and sonocatalytic degradation of caffeine
The sonolytic and sonocatalytic degradation reaction of caffeine solution were carried out in a 250 mL Erlenmeyer flask as a reaction vessel under ultrasonic irradiation. The ultrasonic bath (Elmasonic S 60 H, Germany) was used for this purpose with a frequency and an output power of 37 kHz and 150 W, respectively. The sonocatalytic system was also equipped with two pumps, thermometer and holding tank. Figure 2 shows the schematic diagram of this experimental set-up system. Throughout the process, the temperature of water bath was kept constant at 25±3°C by adding ice cubes in the holding tank in order to avoid the temperature rise in the ultrasonic bath.

For a typical catalytic process, a certain quantity of CeO$_2$ was added to a 100 mL of caffeine aqueous solution with a certain concentration. Prior to the catalyst addition, the pH of the aqueous solution was adjusted using NaOH (0.1 M) or HCl (0.1 M). Then, the suspension was agitated for 30 min in the dark condition to achieve the adsorption-desorption equilibrium. Subsequently, the suspension was added with 20 mM of H$_2$O$_2$ as the oxidant and was sonicated for 150 min in the ultrasonic bath. During the process, 4 mL of sample was withdrawn and filtered through 0.22 µm syringe filter (PVDF) at 30 min of interval time. The absorbance of filtrate was then determined at the maximum wavelength ($\lambda_{\text{max}}$) of 273.5 nm using Lambda 25 UV-VIS Spectrophotometer (Perkin Elmer, USA). Then, the concentration of sample was determined based on the standard calibration curve. Meanwhile, the removal performance for caffeine aqueous solution was calculated as follows: $(C_i - C_f)/ C_i$, where $C_i$ is the initial concentration of caffeine aqueous solution and $C_f$ is the concentration of caffeine aqueous solution after sonication.

![Figure 2](image_url)

**Figure 2.** Schematic diagram of experimental set-up for sonocatalytic system.

2.5. Reusability of CeO$_2$
The reusability of CeO$_2$ was examined for up to three catalytic runs at obtained optimal parameter with similar procedure as stated in Subsection 2.4. After each run, the catalysts were washed, filtered using centrifuged (6000 rpm, 30 min) and dried in an oven at 60°C for six hours. Then, the catalyst was reused with a fresh caffeine aqueous solution for the next run.

3. Results and discussion
3.1. Characterization of CeO$_2$
A typical XRD pattern of CeO$_2$ materials for CeO$_2$ sample is shown in figure 3(a). This catalyst showed intense and sharp diffraction peaks of fluorite cubic structure with $Fm\bar{3}m$ space group (JCPDF no. 00-034-0394) [18]. The diffraction peaks for this sample at 20 values of 28.62°, 33.08°, 47.44°, 56.33°, 59.00°, 69.44°, 76.71° and 78.88° are assigned to (111), (200), (220), (311), (222), (400), (331) and (420) crystal facets of CeO$_2$.

Figure 3(b) exhibits two structural shapes of rod and cube with irregular sizes and diameters. The size of CeO$_2$ sample for rod (diameter, length) and cube are estimated to be 13.9 ± 3.8 x 109.8 ±
18.7 nm and 12.1 ± 3.5 nm, respectively. The findings of this study do not support most of the previous works which only single shape of CeO₂ was supposedly to be formed; rods. However, Piumetti et al. [19] clarified that at a low aging temperature (<150°C) of hydrothermal method, it would lead to the formation of mixed shapes of catalyst. Besides, at high base concentration (6.4 M of NaOH), the Ce(OH)₃ nuclei could become metastable and were oxidized to CeO₂ cube shape which was more stable [17, 20].

The nitrogen adsorption-desorption isotherm curves were also obtained as shown in figure 4(a) for CeO₂. It depicts a typical Type IV physisorption isotherm based on IUPAC that indicates typical mesoporous materials (pore width 2 – 50 nm) [21]. The CeO₂ demonstrates a narrow hysteresis loop reflecting the presence of more porous structure [22]. From the hysteresis loop also, the shape of CeO₂ can be correlated with shape of cylindrical pores (Type A) [23–24]. Meanwhile, the specific surface area (S_{BET}) and pore volume of the catalyst are 126.63 m²/g and 0.4898 cm³/g, respectively. The result of S_{BET} clearly shows that the mixed structural shapes of CeO₂ higher compared to single shape of CeO₂ rod and cube [17]. Therefore, it indicates that the mixed shapes of CeO₂ increased the availability of more active sites on the catalyst surface for adsorption of caffeine molecules.

![Figure 3(a). XRD pattern and (b) TEM image of CeO₂.](image)

**Figure 3(a).** XRD pattern and (b) TEM image of CeO₂.

![Figure 4(a).](image)

**Figure 4(a).** Nitrogen adsorption-desorption isotherms of CeO₂ (b) Effect of solution pH on sonocatalytic degradation of caffeine (Experimental conditions: [CAFF] = 5 mg/L, [CeO₂] = 1.0 g/L, [H₂O₂] = 20 mM).
3.2. Sonocatalytic degradation of caffeine

3.2.1. Effect of pH. Figure 4(b) shows sonocatalytic degradation of caffeine using CeO$_2$ at three different pH values. The sonocatalytic activity of caffeine was enhanced at pH 7.5 in which caffeine was degraded by about 91.5% and it decreased significantly at low pH (pH 3.5) [25]. The effect of pH on degradation of caffeine depend on the point zero charge (pZC) of CeO$_2$ and the ionization of caffeine molecules in aqueous solution. Since the pZC of CeO$_2$ is 6.95 [26], the catalyst surface is positively charged (adsorption of anionic molecules is favorable) when the caffeine solution was at pH < 6.95 and is negatively charged (adsorption of cationic molecules is favorable) when the pH > 6.95. In addition, the molecules of caffeine are fully protonated at pH<10.4 (pKa$_{\text{caffeine}}$) [5]. Therefore, the best sonocatalytic degradation of caffeine could be observed at pH 7.5 due to the adsorption enhancement of caffeine molecules on the CeO$_2$ that was favored at pH between 6.95 and 10.4. In addition, this result also clearly demonstrated that the effect of pH was significant in near-neutral solution in degrading the caffeine.

3.2.2. Effect of initial concentration of caffeine. Effect of initial concentration of caffeine (in the range of 5 – 30 mg/L) on the sonocatalytic degradation using CeO$_2$ was investigated and the result is shown in figure 5(a). Three initial caffeine concentrations of 5, 10 and 15 mg/L experienced the significant degradation within 150 min especially for 5 mg/L (91.5%). However, the caffeine degradation decreased drastically to 19.8% when the initial concentration was 30 mg/L. The sonocatalytic activity was observed ineffective when the concentration of caffeine is higher than 15 mg/L [8]. This can be explained by the fact that at high initial caffeine concentration, more caffeine molecules were adsorbed on the surface of CeO$_2$ to result in fewer active sites for adsorption of hydroxyl ions. Thus, the generation of OH radicals (reactive species) would be decreased leading to low degradation efficiency of caffeine [27]. From this finding, it was demonstrated that the sonocatalytic degradation of caffeine was influenced by its initial concentration. Overall, the highest activity of sonocatalytic degradation of caffeine was found at initial concentration of 5 mg/L which is in agreement with several previous studies which they applied low range of initial caffeine concentration (2.5 – 30 mg/L) in their studies [5, 8, 27].

Figure 5(a). Effect of initial concentration of caffeine on sonocatalytic degradation of caffeine (Experimental conditions: pH = 7.5, [CeO$_2$] = 1.0 g/L, [H$_2$O$_2$] = 20 mM) (b) Effect of CeO$_2$ dosage on sonocatalytic degradation of caffeine (Experimental conditions: [CAFF] = 5 mg/L, pH = 7.5, [CeO$_2$] = 1.0 g/L, [H$_2$O$_2$] = 20 mM).
3.2.3. Effect of CeO$_2$ dosage. The influence of CeO$_2$ dosage on degradation of caffeine was examined by varying the catalyst amount from 0.5 to 2.0 g/L (figure 5(b)). From this figure, the optimal dosage for degradation of caffeine was 1.0 g/L (95.5%) which was relatively higher compared with other dosages. Better dispersion of CeO$_2$ was achieved due to the turbulence generated by ultrasonic induced cavitation at this dosage [28]. This result also suggested that the other CeO$_2$ dosages (lesser or more than 1.0 g/L) had comparatively lower degradation efficiency with not more than 50% of degradation. This can be explained when the dosage was insufficient, lesser nuclei would be generated in the cavitation effect which lead to the fewer •OH radicals generated by the CeO$_2$. On the other hand, when the CeO$_2$ was in excess amount, it would lead to the shielding effect among the particles and interference to the ultrasonic irradiation. Thus, the generation of •OH radicals would be affected [8] leading poorer degradation efficiency of caffeine.

3.3. Comparison of different processes for degradation of caffeine

Figure 6(a) shows the caffeine degradation as a function of irradiation time. The degradation of caffeine was insignificant for the absorption process which almost no degradation achieved within 150 min. Meanwhile, when the ultrasonic radiation was applied, the degradation increased to 13.1% and increased further to 24.1% when H$_2$O$_2$ was added as the oxidant [8]. This result demonstrated that there was a slight phenomenon of sonolysis occurred when this irradiation was used in both systems. As expected, the caffeine degradations further increased when CeO$_2$ was applied simultaneously in conjunction with ultrasonic radiation either with (95.5%) or without oxidant (86.3%). This could be related to the hydroxyl free radicals (•OH) production as the reactive species [16]. As consequent, sonolysis alone with or without the oxidant was not sufficient to degrade caffeine.

3.4. Reusability of CeO$_2$

After three cycles, a negligible decrease in degradation of caffeine was observed (figure 6(b)), highlighting that the CeO$_2$ exhibited high sonocatalytic activity even in the third cycle (81.4%). The reused CeO$_2$ showed a similar efficiency to the fresh catalyst, indicating the stability and reusability potential of CeO$_2$. This result might indicate the future potential application of CeO$_2$ in industrial process.

Figure 6(a). Comparison of different processes for degradation of caffeine in the presence of CeO$_2$ with or without ultrasound and H$_2$O$_2$ (b) The reusability of CeO$_2$ (Experimental conditions: [CAFF] = 5.0 mg/L, pH = 7.5, [CeO$_2$] = 1.0 g/L, [H$_2$O$_2$] = 20 mM).
4. Conclusions

In summary, CeO$_2$ was successfully synthesized using the hydrothermal method. The results indicated that the sonocatalytic degradation of caffeine was obviously affected by pH, initial concentration of caffeine and dosage of CeO$_2$. In general, the degradation efficiency was found to increase with a decrease in initial concentration of caffeine and dosage of CeO$_2$ at near-neutral solution. The highest degradation of caffeine (95.5%) was achieved in 150 min at a pH of 7.5, 5.0 mg/L of initial concentration of caffeine and 1.0 g/L of CeO$_2$ dosage. The sonocatalytic process using CeO$_2$ showed great potential in treatment of caffeine. In addition, CeO$_2$ could be applicable to the practical application since it showed high stability and reusability.

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