

Photocatalytic Degradation of Allopurinol using Cerium Oxide

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Abstract - Allopurinol (AP) is an antigout drug under the brand names Zyloprim and Zyloric. It is a structural isomer of hypoxanthine, a naturally occurring purine in the body which inhibits xanthine oxidase that results in decrease in uric acid formation. In this work, degradation of aqueous solution of Allopurinol by photocatalysis was studied using CeO₂. The CeO₂ was synthesized by Co-Precipitation method and it was characterized by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDAX), FTIR and BET Surface Area Analyzer. FTIR confirms the finger print region for CeO₂ around 829.92 cm⁻¹. Surface area of CeO₂ was measured as 64.42 m²g⁻¹ by BET surface area analysis. The optical and thermal stability was determined using DRS UV-Visible spectroscopy and Thermo gravimetric analysis. In this study the concentrations of Allopurinol was quantified using UV-Visible Spectroscopy. The feasibility of photo degradation of allopurinol using CeO₂ was carried out in the presence of UV irradiation of 254 nm. The optimization of process control parameters such as catalyst dosage, pH and allopurinol concentration was assessed. From the assessment, degradation rate decreases with increase in initial concentration of Allopurinol whereas it increases with increase in CeO₂ concentration up to 0.04 g/l. In case of pH, degradation constant increases with increase in pH from 8.5 to 11.

Keywords: Allopurinol, Cerium oxide, Characterization, Photocatalysis

I. INTRODUCTION

In recent days, several pharmaceutical compounds have been used due to rapid growth in population and advancement in medical science. Mostly pharmaceutical waste compounds from pharma industries and household activities are directly discharged into water bodies. As a result, gradual increase of pharmaceutical compound is observed in the surface as well as ground water bodies.

It is difficult to separate and degrade various formation of pharma compounds (i.e. antibiotics, steroids etc.,) through conventional treatment. Allopurinol (AP) (2,4-dihydroxypyrazolo [3,4-d]pyrimidine) is a drug has been primarily used to treat hyperuricemia and its complications including chronic gout. It is an inhibitor of the enzyme xanthine oxidase which is responsible for the successive oxidation of hypoxanthine and Xanthine, resulting in the production of uric acid, product of human purine metabolism [1]. Molecular formula is C₅H₄N₄O and the molecular weight is 136.112 g/mol.

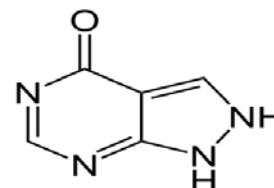
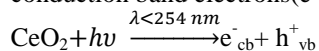
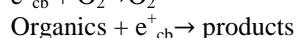
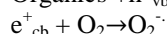
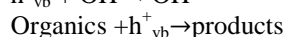
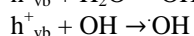
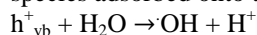


Fig. 1 Structure of Allopurinol

Allopurinol is almost completely metabolized to oxypurinol within two hours of oral administration and it is slowly excreted by the kidneys over 18–30 hours [2]. Elimination of Allopurinol from wastewater is an important issue. For this purpose, Advanced Oxidation Process (AOPs) is considered as a promising option to treat waste water containing AP due to complete mineralization of parent materials. Generally AOPs involve generation of hydroxyl radicals through UV/Photocatalyst, UV/H₂O₂ and UV/O₃ process. In these methods, Photocatalyst reaction using CeO₂/UV can treat non-biodegradable organic compound into biodegradable species. Also it can use as a pre or post treatment process in wastewater treatment process because of its easy installation in conventional wastewater treatment [3]. In this paper, Cerium Oxide (CeO₂) was selected as a catalyst in the photocatalytic removal of AP. CeO₂ was synthesized by Co-Precipitation method. Characterization was investigated by TG, FTIR, DRS-UV Vis, SEM and BET-SAA. Effects of process control parameters including pH, CeO₂ dosage and AP concentration on photocatalytic degradation of AP were investigated. Reaction mechanisms of photocatalytic processes have been discussed extensively in the literature [4]. In detail, illumination of aqueous CeO₂ suspension with irradiation energy greater than the band gap energy (E_{bg}) of the semiconductor generates valence band holes (h⁺vb) and conduction band electrons (e⁻cb).



The photogenerated valence band holes and conduction band electrons can recombine to liberate heat or make their ways to the surface of CeO₂, where they can react with species adsorbed onto the catalyst surface.



Produced hydroxyl radicals (OH) along with other oxidants, e.g., superoxide radical anion can further mineralize organic compounds to end products (water and CO₂). In this study, photo degradation of Allopurinol in aqueous CeO₂ suspension using UV irradiation of 254 nm was studied to determine optimal remove conditions with respect to allopurinol concentration, Catalyst loading and pH.

II. EXPERIMENTAL PROCEDURE

A. Materials and Method

1. Chemicals and Reagents

Analytical grade of cerium nitrate, sodium hydroxide, sodium acetate, acetic acid, hydrochloric acid, and ethanol was obtained from Merck. Zyloric tablets were taken for study which contains Allopurinol 100mg was purchased from local market. All experiments were carried out with Milli. Qultrapure water system of 18.2Ω resistivity.

2. Instrument

An electronic weighing balance (0.1mg sensitivity, Shimadzu AY 220), a sonicator (sonica, model 2200 MH), Bet-Surface Area Analyser (Belsorp mini II), Thermogravimetric Analyser (Shimadzu), FTIR(Perkin Elmer, L160000E), Double beam UV-Visible Spectrophotometer (Perkin Elmer, Lambda35) were used in this study.

3. Synthesis of CeO₂ Nanoparticle

CeO₂ nanoparticle was synthesized using co-precipitation method. 1N Sodium hydroxide is adding dropwise to the precursor 0.1M cerium nitrate which was prepared using deionized water. As soon as NaOH solution was added, a white precipitate Ce(OH)₃ was formed. Then the solution was stirred about 800rpm for 2 hours in an ambient condition. After the complete addition of NaOH, the solution was turned to pink color. It indicates the oxidation transfer of Ce(III) to Ce(IV) Again it was under stirring for about 1200rpm for 5hours. Finally, yellow precipitate started to appear. Then it was centrifuged 10 minutes with 10000rpm and washed with ethanol and deionized water several times to remove excess ions. At last, the products were dried in a hot air oven at 70°C overnight and then calcined for 4 hours at the temperature of 800°C. Thus cerium oxide nanoparticle was obtained.

4. Characterization of CeO₂

The structural morphology, particle size, dispersity and composition of CeO₂ were investigated by Field Emission Scanning Electron Microscope (FESEM) coupled with EDAX. The surface area, pore volume and average pore radius of the sample were measured by Belsorp mini II. The samples were degassed to remove moisture and impurities at 200°C for 4 hours under 50mTorr vacuum and their BET

area, pore volume and average pore radius were determined. The Fourier Transform Infrared spectra of synthesized CeO₂ were recorded at room temperature using KBr pellets on Perkin Elmer L160000E ranging from 4000-450 cm⁻¹.

The UV-vis absorbance spectra of the samples were obtained by Perkin Elmer Lambda35 with glass slit width of 1 nm. The samples were recorded at room temperature in air within the range of 200-700 nm. Thermo gravimetric analysis (TG) analysis was carried out with D-40 analyzer at the rate of 10°C/min under static air condition in the temperature range of 20°C-800°C.

5. Preparation of Stock Solution of Allopurinol

A quantity of 100ppm allopurinol standard solutions were prepared by dissolving 0.1g in 0.1M potassium hydroxide and complete the volume up to 1000mL by deionized water. It makes the stock solution of Allopurinol.

6. Preparation of Working Standard Solution of Allopurinol

From the above standard stock solution, 1ml was pipetted out into a 10mL volumetric flask and the volume was made up to the mark with distilled water to get a concentration of 10 mg/L.

7. Preparation of Calibration Curve

From the working standard solution, 0.1ml, 0.5ml, 1ml, 2.0ml, 3.0ml, 5ml were pipetted into 10ml volumetric flasks and volume was made upto the mark with distilled water to produce the concentrations ranging from 1 to 50 mg/L respectively. The analytical wavelength was selected in the wavelength range of 700-200nm using distilled water as a blank and the wavelength corresponding to maximum absorbance (λ_{max}) was found to be 250.6nm and the corresponding UV spectrum was shown in the figure 2 Then, the calibration curve was plotted in the concentration range of 1-50 mg/L at 250.6nm by taking concentration on X- axis and absorbance on Y-axis. The correlation coefficient (r²) was found to be 0.997. The calibration curve of allopurinol was shown in Fig. 2.

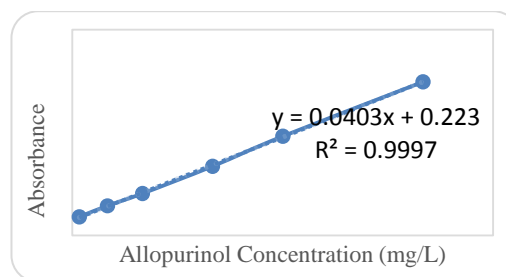


Fig. 2 Calibration graph for Allopurinol (1 to 50 mg/L)

8. Experimental Setup

Photocatalytic reactor used for Allopurinol degradation was shown in Fig 3. It consists of 6 Sample holder with capacity

of 75ml each, UV lamp for light source (254 nm, 365 nm). The solution in the reactor was constantly stirred using air plunger. An artificial UV lamp emitting maximum wavelength of 254 nm is used for this experiment. The whole experiment was conducted in a batch mode.



Fig. 3 Photocatalytic Reactor

9. Experimental Procedure and Analysis

In batch experiment, a selected dosage of CeO_2 from 0.01 g/L to 0.05g/L added to 1000 mL of AP solution with certain concentration (10mg/L to 50 mg/L) at different pH range from 3 to 11. Initial pH of the solution was adjusted by NaOH and HCl and measured by pH meter. All runs were performed under ambient conditions for 2 hours. During the experiment, solution in the photoreactor under continuous air supply and kept at constant temperature. The AP solution loaded with CeO_2 was equilibrated under dark for 30 min. After the equilibrium period, UV lamp is switched on and 5ml of the solution was taken at distinct time intervals. The aqueous sample was filtered to eliminate CeO_2 and then calculate concentration of the residual solution.

The absorbance of the supernatant was measured at the maximum absorbance of Allopurinol ($\lambda = 250 \text{ nm}$) by UV-vis spectrophotometer to calculate the degradation rate of Allopurinol.

$$D_e = \left(1 - \frac{A}{A_0}\right) * 100\%$$

Where A is the final absorbance and A_0 is final absorbance of the solution. The degradation rate of the Allopurinol solution was used to characterize the photocatalytic activity of CeO.

III. RESULTS AND DISCUSSION

A. FESEM/EDAX Analysis

The formation of nano- CeO_2 was confirmed by SEM with EDAX. A representative SEM image Fig. 4 shows that, the most of the particles are well distributed. From the image, it is shown that the particles formed in rod shape. Cerium

oxide particles tend to agglomerate, as is typical of nanoparticles. The average size of the CeO_2 was around 87 nm. The quantitative compositional analysis of CeO_2 was carried out using EDAX spectroscopy measurements. EDAX spectrum has been shown in Fig 5. It showed the composition of Ce, O and Na as 56.04%, 18.32% and 13.48% by weight i.e. minimum level of impurities were present in nano- CeO_2 .

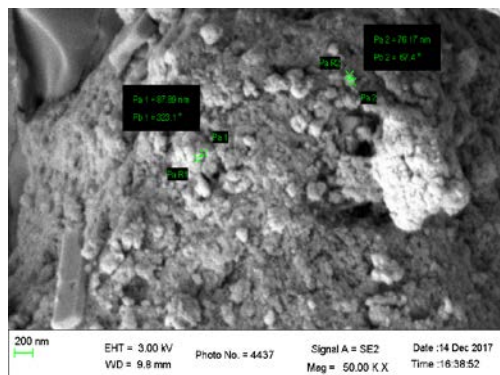


Fig. 4 SEM Image of Cerium Oxide

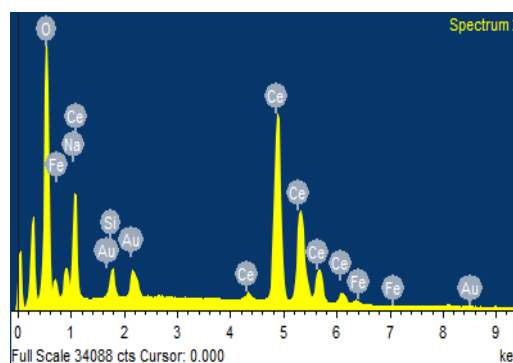


Fig. 5 EDAX spectra of CeO_2

B. FTIR Analysis

Fig. 6 shows the FT-IR spectra of CeO_2 nanoparticle. The Peak at 3500 cm^{-1} corresponds to -OH Stretching of H_2O . Peak in range of $1300 \text{ cm}^{-1} - 1800 \text{ cm}^{-1}$ indicates the carbonate ion stretching vibration i.e. physical adsorption of water molecules. The Ce-O stretching band around 829.92 cm^{-1} confirms the fingerprint region of formation of cerium oxide nanoparticle.

C. BET Surface Area Analysis

Fig. 7 shows the nitrogen adsorption-desorption isotherms at temperature 77 K. The isotherm of sample reveals the stepwise adsorption and desorption plot of type IV isotherm, typical mesoporous materials. The desorption branch of the isotherm follows the same path to the adsorption branch.

The BET surface area and porosity of the sample was found to be $64.42 \text{ m}^2/\text{gm}$. In addition the pore volume and pore diameter was measured to be $0.1244 \text{ cm}^3/\text{gm}$ and 7.413 nm respectively.

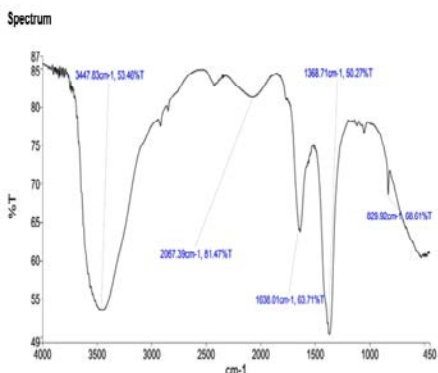


Fig. 6 FTIR Spectrum of CeO₂

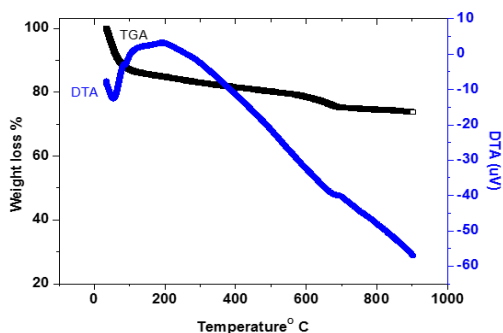


Fig. 8 TG Curve of CeO₂

D. TG Analysis

TG curve of cerium oxide was shown in Fig8. TG analysis was carried at an oxidizing atmosphere by using air. Black line represents TGA, it showed the weight loss of CeO₂nanoparticle for different temperature. The process of weight loss can be divided into 2 steps.

1. First straight peak from around 60°C to 100°C is due to dehydration of cerium nitrate precursor and the formation of anhydrous nitrate. The weight loss of the precursor is 13%.The second slight change from around 100°C to 630°C is due to the dehydration of anhydrous nitrate to formation of CeO₂ nano crystalline. The weight loss is 10%.
2. After 620°C, the weight of precursor has no longer changes, which indicates that the precursor has completely decomposed and crystalline CeO₂ has formed completely.
3. According to TG analyses, calcined temperature should be above 630°C in order to obtain pure CeO₂.
4. Thus, the composition of precursor is CeO₂ 76%, CO₂ 10%and H₂O 13%.

Blue line represents DTA, it explains the exothermic and exothermic reactions takes place in the nanomaterial.

1. Downward peak represents Endotherm reaction around 80°C -130°C is due to the loss of bulk water and hydrate water.
2. however, the exothermic peak in the temperature range of 120°C to 380°C indicated that the decomposition of cerium nitrate and the exothermic oxidation of Ce (III) by O₂ to Ce (IV).

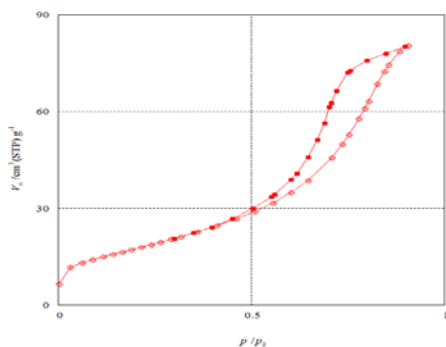


Fig. 7 N₂ Adsorption - Desorption Isotherm

E. DRS UV-Vis Spectroscopy

The maximum peak obtained from the DRS UV-VIS graph (λ_{max}) is 387.30 nm at 0.95 Å was shown in the Fig. 9. Band gap can be calculated using the formula,

$$E=h \cdot C/\lambda$$

Where, Energy (E) = Band gap, Planks constant (h) = 6.626×10⁻³⁴ Joules sec, Velocity of Light (C) = 2.99×10⁸ meter/sec and Wavelength (λ) = 387.3 nm. Also 1eV = 1.6×10⁻¹⁹ Joules (Conversion factor).

Energy bang gap width is calculated for the resulted maximum peak of 387.3 nm is 3.22 eV.

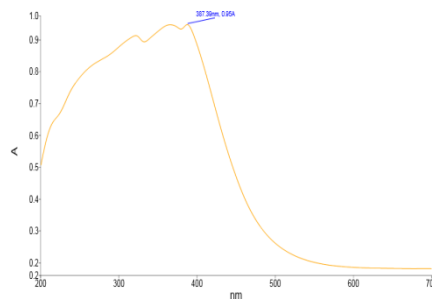


Fig. 9 UV-vis Spectrum of CeO₂

F. Effect of Adsorption

Adsorption studies were carried out by varying CeO₂ loading in the range from 10 mg/L to 60 mg/L with constant concentration at pH 8. The experiment was carried under dark for 1 hour. The experiment results showed negligible removal. So the effect of adsorption was neglected in the following experiments.

G. Effect of Catalyst Loading on Photocatalysis

Photo catalytic degradation of Allopurinol was examined at different concentration of CeO₂ ranges from 10 mg/L to 60 mg/L. The other parameters made constant with Allopurinol concentration of 30ppm at pH 8. The degradation efficiency was shown in Fig 10. Degradation time increases, the degradation efficiency increases with increase in initial concentration of CeO₂till 40 mg/L and decreases gradually i.e. with increase in CeO₂ concentration the large number of

particles are entitiled by the UV light and degradation increases till 40 mg/L. On further increasing the concentration, turbidity of the solution increases which affects the light penetration and the efficiency falls rapidly. The optimum catalyst loading of 40 mg/L was chosen to carry out the following experiments.

H. Effect of pH on Photocatalysis

The effect on pH was investigated by adjusting pH values from 3 to 11 at constant Allopurinol concentration and catalyst loading of 40 mg/L. Fig. 11 showed the degradation efficiency. The degradation rate decreases at pH less than 7 and it increases after 7. The degradation efficiency was maximum at 9 and it started decreased. The degradation efficiency increases at higher pH because it contains more hydroxyl ions which naturally increase the degradation efficiency whereas the degradation rate decreases at pH 11.

This is due to surface ionization. The point of zero charge of CeO_2 is 7.2 and the pK_a of Allopurinol is 10.25. The CeO_2 exhibits positive charge when $\text{pH} < 7$ and it exhibits negative charge when $\text{pH} > 7$. Similarly, Allopurinol shows positive charge below $\text{pK}_a=10.25$. Hence there exists a static repulsion till $\text{pH}=7.2$ and also after $\text{pK}_a= 10.25$. Thus the efficiency of degradation falls. The effect of adsorption has been neglected earlier. Hence the degradation rate of Allopurinol is efficient between pH 7 to pH 11.

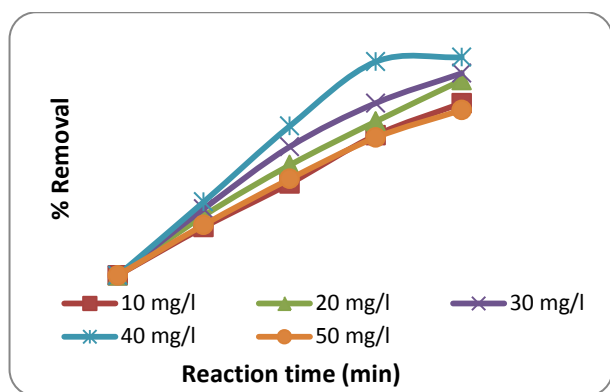


Fig. 10 Effect of CeO_2 Loading on the Photo Catalytic Degradation of Allopurinol with Initial Concentration of 30 mg/l (Initial pH=8)

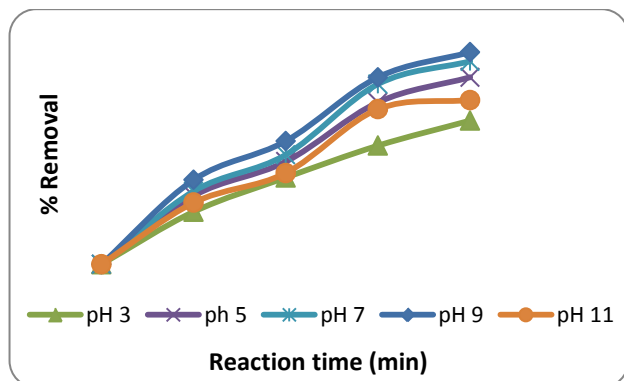


Fig. 11 Effect of pH on the Photo catalytic degradation of Allopurinol with initial concentration of 30 mg/l (Optimum CeO_2 loading 40 mg/l)

I. Effect of Initial Concentration on Photo Catalysis

The degradation rate decreased when the initial concentration of Allopurinol increased from 10 to 50 mg/L. Fig. 3 showed the degradation efficiency with the effect of initial concentration. The rate of degradation decreased with increased in Allopurinol concentration. This may be resulted with the shortage of the reactive species. With increasing Allopurinol concentration, there exists a competition with the reactive species which decreases the degradation efficiency.

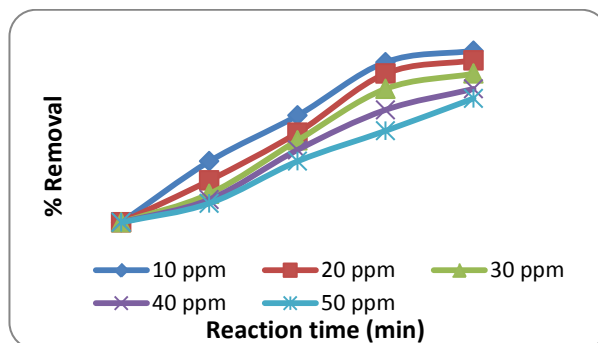


Fig. 12 Effect of Initial Concentration on the Photo Catalytic Degradation of Allopurinol with Optimum pH 9 and CeO_2 loading 40 mg/l

IV. CONCLUSION

Cerium oxide nanoparticles were synthesized using Co-precipitation method. The morphology, size and chemical composition were characterized using FESEM/EDAX. The FTIR spectrum indicated the presence CeO_2 nanoparticles. UV spectra of synthesized CeO_2 were measured. It has strong absorbance at the wavelength of 387 nm. Hence it was used as the catalyst for photo degradation of Allopurinol. A simple spectrophotometric method for the quantitative determination of Allopurinol in tablet form was developed. It was carried out at room temperature at a maximum wavelength of 250 nm. The experimental results showed that the degradation rate increases with high CeO_2 loading and maximum degradation rate was obtained at concentration of 40 mg/L of CeO_2 . After that, it decreased gradually. The reason is that excess CeO_2 increases the turbidity which minimise the degradation rate. The degradation efficiency increased slightly with increase in pH from pH 7.2 to pH 10.25. This is due to enhanced formation of hydroxyl ions. However at pH below 7.2 and above 10.25 electrostatic repulsion between CeO_2 surface and Allopurinol retard the degradation efficiency. Degradation rate decreases with an increase in initial concentration of Allopurinol.

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