

Photochemical degradation of pharmaceuticals experiment



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Experimental Methodology

Experimental methodology executed for accomplishment of a project is one of the most important parts of study, deciding the ultimate outcomes of the study. For the present study It aimed at metal doped MCM-41 for the removal of pharmaceuticals by their degradation under UV irradiation. The present investigation was therefore designed to avoid discrepancies as much as possible, and to maximize the outcomes.

The photochemical degradation of pharmaceuticals has become an important index in ecological environment safety evaluation of drugs. To elucidate the photodegradation profiles of drugs in the environment, many investigators have focused on solution photolysis in organic solvents or in a dilute aqueous solution. The present study was based on photo degradation of two commonly used pharmaceuticals i. e., salts of diclofenac and atorvastatin in different solvents. Another perspective of the present study was to determine the metal doped mesoporous silicates materials as catalyst for the photo degradation of pharmaceuticals under UV radiations, sunlight and in absence of light.

The details of the experimental methodology adopted are spelled out as under:

3. 1 The glassware/ volumetric Apparatus

The proper and appropriately cleaned and calibrated glassware and volumetric apparatus is necessary for accurate and precise analytical measurements. Thus, high quality pyrex glass-ware was used during the

course of experiment. This apparatus was given through wash with detergent solution, diluted HNO_3 and finally with distilled water. All the glassware used was dried at 100°C in an electric oven before use. All the apparatus like beakers, measuring flasks, pippets and graduated cylinders were calibrated prior to use.

3. 2 The Reagents

Synthesis of mesoporous silica, metal doping on synthesized mesoporous material and degradation studies required various reagents. In addition to other parameters, the success of experimental methodology also depended on their purity and quality. So in order to ensure quality analytical grade chemicals which were purchased from Uni-chem (China), E. Merk (Germany), Riedel-deHaen (China) and Sigma Aldrich were used.

Sodium silicate, cetyltrimethyl ammonium bromide (CTAB), H_2SO_4 , $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and copper acetate were obtained from sigma Aldrich with a certified purity of 99.9%. In order to avoid any photo degradation, all the reagents were kept in dark.

3. 3 Equipments/ instruments used

a. The following equipments were used for the successful completion of the present study.

Magnetic stirrer/ Hot plate

Oven

Shaker

Muffle furnace

UV-irradiator

pH meter

b Instrument Used

UV- Visible Spectrophotometer

The spectro photometric measurements were performed on a UV-visible double-beam spectrophotometer (U-2800). It operates on the principle of measurement of the intensity of light after passing through a sample (I) and comparing it to the intensity of light before it passes through the sample (I_0). The ratio (I/I_0) is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A is calculated by the following equation:

$$A = \log (100/\%T)$$

The basic compartment of a spectrophotometer include; light source, sample holder, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector. The radiation source is often a tungsten filament (300-2500nm) and a deuterium arc lamp, which is continuous over the ultraviolet region (190-400nm). More recently, light emitting diodes (LED) and xenon arc lamps for visible wave length have also been incorporated. The detector is typically a photodiode or CCD (charge couple device detector to enhance the uv spectrophotometer performance).

Photodiodes present with monochromators filter the light so that only light of

single wavelength reaches the detector. Diffraction gratings with CCDs collect light of different wavelength on different pixels.

$$\log_{10} I_0/I = \epsilon c l$$

ϵ = greek letter, epsilon

l = length of solution the light passes through (cm)

c = concentration of solution (mol dm^{-3})

The expression $\log_{10} I_0/I$ is known as the absorbance of the solution and is measured by the spectrometer.

For the present study the UV spectrophotometer was used for determining the degradation of different pharmaceutical products under different conditions. For this purpose the absorbance of diclofenac sodium was recorded at a wavelength of 276 nm and that of atorvastatin was recorded at wavelength of 246 nm.

cBruker alphaATR spectrophotometer

The Platinum ATR is a single reflection diamond ATR sampling module that is designed to significantly ease analysis. The ergonomic one finger clamp mechanism simplifies the sample positioning. The robust diamond crystal allows analyze nearly all kind of liquid and solid samples. For the present study the IR analysis of MCM-41, Cu/MCM-41 and Ce/MCM-41 was

cSDT-Q600 Thermo Gravimetric Analyser

The TA Instruments SDT-Q600 Simultaneous TGA / DSC provides simultaneous measurement of weight change (TGA) and true differential heat flow (DSC) on the same sample from ambient to 1, 500 °C. It features a field-proven horizontal dual beam design with automatic beam growth compensation, and the ability to analyze two TGA samples simultaneously.

For the present study the thermogravimetric analysis of mesoporous silicate was:

3. 2 Analytical Methodology

3. 2. 1 Preparation of mesoporous silica

For the preparation of mesoporous silica the method of Taron et. al was used.[i]In this method the sodium silicate was used as a source of silica and cetyltrimethyl ammonium bromide (CTAB) used as a surfactant. Briefly, a 15.75g part of sodium silicate was dissolved in 45.75g of DDW and stirred for 15 minutes at room temperature in a poly propylene container (A). A 13.535g of CTAB was separately dissolved in 200 ml of doubly distilled water at room temperature to prepare an aqueous solution of CTAB (B). To a stirred solution of precursor (A), the template solution (B) was added drop wise. After the completion of addition, the solution was further stirred for about 1h. Subsequently the pH of the contents was maintained at 10.5 by using 1: 1 H₂SO₄, (6.7ml) which yielded a gel that was further stirred for about 45 minutes. The polypropylene container was then sealed and allowed to age for twenty four hours at room temperature without stirring. The gel thus obtained was filtered, washed with doubly distilled water to get rids of ions

present as impurities and dried in an electric oven at 120 ° C. Thus dried product was allowed to calcine at a heating rate of 3 ° C/min for 6 hours while maintaining a maximum temperature of 550 ° C. The product obtained after calcinations was mesoporous silica MCM-41, that was used for further experiments.

3. 2. 2 Metal impregnation of mesoporous silica

a) Preparation of CeO₂/MCM-41

Li et. al method was adopted for the synthesis of MCM-41/CeO₂. [ii] This is based on grinding of precursors. In this method, 0.6402 g of (NH₄)₂Ce(NO₃)₆ and 0.3g of synthesized MCM-41 were placed in a mortar and ground significantly at room temperature conditions. The obtained solid was calcined at a heating rate of 5 ° C/min until the maximum temperature obtained 550 ° C in air for 3 to 4 h to remove the surfactant molecules [iii]

b) Preparation of copper supported mesoporous silica (Cu/MCM-41)

The copper was loaded on the mesoporous support material through wet impregnation of silica. 2g of silica was stirred in 0.025M of 20mL copper acetate for 24 hours at room temperature. The copper impregnated silica was washed with distilled water to remove free copper and acetate ions and then dried at 70 ° C for 12h. The copper impregnated silica was calcined at 600 ° C for 4 h to get silica supported copper sample (Cu-MS). [iv]

c) Preparation of Cu-doped MCM-41 with different percentages:

The MCM-41 mesoporous powder material after drying at 120 °C over night was impregnated with solutions of different concentrations separately under continuous stirring for 12 h at room temperature, and then they were dried at 100 °C. The obtained materials were calcined in air from room temperature to 150 °C at 5 °C/min and held at 150 °C for 1 h, and then heated from 150 °C to 250 °C at the rate of 5 °C/min and held at 250 °C for 1 h, at last heated from 250 °C to 330 °C at 5 °C/min and held at 330 °C for 2 h. By using this procedure, samples containing 5, 10 and 15 wt% Cu-MCM-41 was prepared.[v]

3. 2. 3 Degradation studies

Preparation of Pharmaceuticals Standards

Pharmaceuticals Stock Solution Preparation

A primary standard solution of pharmaceuticals with concentration 1000 ppm was prepared by dissolving 0.1 g of pharmaceuticals in 100 mL of solvent. The solution was kept in refrigerator at 4 °C prior to use.

Pharmaceuticals Spiking Solution Preparation

The intermediate standard solutions of pharmaceuticals were prepared by diluting 0.5, 0.4, 0.3, 0.2 and 0.1 mL of 1000 ppm of stock solution upto 10 mL of solvent to prepare 50, 40, 30, 20 and 10 ppm of standards.

1. Effect of light
2. Effect of time
3. Effect of metal
4. Effect of metal loading levels

5. Effect of pH

REFERENCES:

[i]H. W. Lee , H. J. Cho , J. H. Yim , J. M. Kim , J. K. Jeon , J. M. Sohn , K. S. Yoo , S. S. Kim , Y. K. Park , Removal of Cu(II)-ion over amine-functionalized mesoporous silica materials, Journal of Industrial and Engineering Chemistry (17) 504-509(2011)

[ii]H. R. Pouretedal, M. Ahmadi, Synthesis, characterization, and photocatalytic activity of MCM-41 and MCM-48 impregnated with CeO₂ nanoparticles, journal of International Nano Letters, 2: 10(2012)

[iii](Li, Y, Yan, B, Functionalized mesoporous SBA-15 with CeF₃ : Eu³⁺ nanoparticle by three different methods: synthesis, characterization, and photoluminescence. Nanoscal. Res. Lett. 5, 701-708 (2010).

[iv]Manish dixit, Manis mishra, P. A. Joshi, D. O. Shah, “ Study on the catalytic properties of silica supported copper catalysts”, journal of procedia engineering, 51, 467-472(2013).

[v]Ye Wan, Chao Chen, Weiming Xiao, Lijuan Jian, Ning Zhang, “ Ni/MIL-120: An efficient metal-organic framework catalyst for hydrogenation of benzene to cyclohexane” , Microporous and Mesoporous Materials 17, 1 9-13(2013).