Synthesis of mesoporous silica mcm-41

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Results and Discussions

The present study included the synthesis of mesoporous silica MCM-41 and its modification by impregnation of different metals on the mesoporous to enhance the photocatalytic activity of metals i. e Cu/MCM-41, Fe/MCM-41, CeO_2 /MCM-41.

FTIR analysis of catalyst

MCM-41 has the ability to impregnate numerous metals on its surface. MCM-41 was modified with metal salts in order to dope the metals on the surface of mesoporous material was characterized by FTIR analysis. The FT-IR spectra furnished the information about the incorporation of metals on the surface of MCM-41. The FT-IR spectra of synthesized material in the region of 4000 – 400 cm-1 in transmission mode using platinium ATR, a single reflection sampling module spectrophotometr, and shown in Fig. 5. The uncalcined MCM41 and calcined MCM41 spectra (Fig. 5A. a, b) show intense band at wavenumber 1100 and 802 cm-1 which accounts for the asymmetric and symmetric stretching of the Si-O-Si bonds, respectively.[i]The bands at 970 cm-1 and 460 cm-1 was assigned to the stretching and bending vibrations of surface Si-O- groups respectively.[ii]The sharp peaks at 2864. 72cm-1 and 2922. 14 cm-1 were due to the presence of surfactant before calcinations of MCM-41.[iii]For calcined MCM41, the bands at 2852 cm-1 and 2921 cm-1 corresponding to the long chain of alkyl group of the surfactant molecules were disappeared after calcination shows the completely removal of surfactants molecules. The differences of the intensities of the peaks in the FT-IR spectra of MCM-41 and MCM-41/ CeO2, are observed which

resulted from the doping of CeO_2 . A strong absorption peak at 1, 632 cm−1 is observed in the spectra of MCM-41/CeO2, and it indicates the formation of Ce-O-Ce.[iv]

About copper and iron also add

TGA analysis of MCM-41:

XRD analysis of MCM-41:

Photocatalytic studies by using the metal dopped MCM-41:

The metal dopped MCM-41 was studied for the photocatalytic degradation of commonly used pharmaceutics including salts of diclofenac (non-steroidal anti-inflammatory drug (NAID)) and atorvastatin (antihyper lipoproteinemic drug). For this purpose the solutions od these drugs were prepared and degradation potential of metal dopped mesoporous silicate was studied by optimizing various parameters i. e the amount of catalyst, the pH, the light, substrate concentration, metal loading on MCM-41.

Effect of pH

The interaction between the pharmaceutics and metal dopped mesoporous are dependent on the pH of the solution therefore the optimization of pH is important to achieve maximum degradation efficiency. During the present study, the degradation process was optimized by changing the pH from 3. 5 to 10. 5 over 10 wt% M/MCM-41(M= Cu, Fe, Ce) with 1 g l_{-}^{-1} of 0. 114 mM drug solution. The pH of the pharmaceutic solution is adjusted with 0. 1 M HCl and 0. 1 M NaOH. The results obtained are shown in Fig. 3d. At acidic pH,

the rate of degradation is faster as compared to high and neutral pH. The results clearly show that acidic pH is ideal for the degradation of the pharmaceutics.

Effect of light intensity on degradation of pharmaceutic:

The photolysis of pharmaceutic was studied under UV irradiation and dark. The log natural decay curves (In Ct/Co) of pharmaceutic versus irradiation time were displayed in (Fig. 3-5). The data for dark control samples were also elaborated in Fig. 6. Photodegradation of diclofenac sodium and atorvastatin under UV light in distilled water and methanol respectively were determined during the summer season (March-september) as displayed in Fig. 3. The determined half life of 50 ppm diclofenac sodium in distilled water under UV light was 2. 5h and in dark it was observed as 3 h.

The rate of reaction varied from $2.\ 8\times10^{-3}$ to $2.\ 3\times10^{-3}$ when pharmaceutic was shifted from UV light to dark.

Effect of metal loading on MCM-41

The effect of metal loading over MCM-41 on the photocatalytic activity is investigated and the results are shown in Fig. 2a. The degradation studies are carried out with increase of metal (wt%)5, 10 and 15 using 1 g l^{-1} of catalyst amount in 50 ml pharmaceutics solution. It is observed that 5–10 wt % increase in metal loadings, the photocatalytic activity increases and there is not much degradation rate at higher loadings. Among all the catalysts, 10 wt% M/MCM- 41 (M= Cu, Fe and Ce) showed most efficient photocatalytic degradation of pharmaceutics i. e., complete degradation within 90 min. The

loss in the activity with increase in metal percent loading is due to the excess amount of metal oxide dispersed over MCM-41 that blocks the mesopores results a decrease in adsorption capacity. The turbidity of the solution also blocks penetration of light into the solution. Thus, the metal loading over the support clearly shows that one has to optimize the metal content, simultaneously retaining the active sites for adsorption in order to achieve the effective synergism.

Effect of catalyst amount

To optimize the amount of catalyst required for effective pharmaceutic photocatalytic degradation, different catalyst amounts (0. 25–1. 5 g l^{-1}) are studied with 10 wt% M/MCM-41 and the results are shown in Fig. 3a. It is observed that 1. 0 g l^{-1} is found to be the optimum. By increasing 0. 25– 1. 0 g l^{-1} , the photocatalytic activity is increased and at higher contents the activity is not beneficial. This may be due to the fact that higher amount of the catalyst is obstructing the path of light penetration into the solution (i. e., scattering of light) thus reducing the OH radicals formation.

Effect of substrate concentration

The effect of 0. 094, 0. 1571 and 0. 2829 mM pharmaceutics concentrations are performed over 10 wt% M/MCM-41 catalyst with 1 g l^{-1} amount for degradation. From Fig. 3b, it is observed that at lower concentrations, the adsorption is more compared to higher concentrations. There is a slight difference in degradation at 0. 094, 0. 1571 mM concentrations in comparison to 0. 2829 mM. Also, it is acknowledged that the degradation is

solely depends on the OH radical formation. The production of OH radicals is not sufficient in comparison to the amount of pharmaceutic adsorbed on the surface of the photocatalyst at higher concentrations. In view of this it suggests that, there should be equilibrium between adsorption of reactant molecules and OH radicals generated from the active sites. The 0. 1571 mM concentration of pharmaceutic is found to be optimum for 10 wt% M/MCM-41 catalyst using 1 g l^{-1} amount. The experimental kinetic data are presented in Fig. 3c (inset) and in Table 1, along with time required for 50% degradation (t1/2) for each of the fitted lines. The degradation rate of pharmaceutic is decreased while increasing the concentration.

The rate constant ‘ k’ decreases with increase in initial concentration of drug. The effect of initial concentration of pharmaceutic on the photocatalytic degradation rate is described by pseudo-first order kinetics. The apparent rate constant for 0. 114 mM IPU over 10 wt% TiO2/Al-MCM- 41 catalyst is 0. 072 min^{-1} (R2 = 0. 994). In the present investigation, 0. 1571 mM concentration is found to be the optimum for degradation studies.

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[ii]

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