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# Enhanced photocatalytic and adsorptive degradation of organic dyes by mesoporous Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41: intra-particle mesoporosity, electron transfer and OH radical generation under visible light

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Mesoporous Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 composite was synthesized by two step processes; *in situ* incorporation of high surface area mesoporous Al<sub>2</sub>O<sub>3</sub> (MA) into the framework of MCM-41 (*in situ* method) followed by impregnation of Cu(II) by incipient wetness method. The interesting thing is that starch was used for the first time as template for the preparation of high surface area MA. To evaluate the structural and electronic properties, these catalysts were characterized by low angle X-ray diffraction (LXRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), UV-vis DRS, FTIR and photoluminescent (PL) spectra. The various cationic dye such as methylene blue (MB), methyl violet (MV), malachite green (MG) and rhodamine 6G (Rd 6G) of high concentration 500 mg L<sup>-1</sup> were degraded and adsorbed very efficiently (100%) using the 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 composite within 30 and 60 min, respectively. The high and quick removal of such concerted cationic organic dyes and also mixed dyes (MB+MV+MG+Rd 6G) by means of photocatalysis/adsorption is basically due to the combined effect three characteristics of synthesized mesoporous 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 composite. These characteristics are intra-particle mesoporosity, electron transfer and 'OH radical generation under solar light.

# Introduction

Organic dyes are one of the notorious contaminants in aquatic environments because of their huge volume of production from industries, slow biodegradation, decoloration and toxicity.1 Over 700 000 tons of dyes and pigments are produced annually worldwide, of which about 20% are in industrial effluent from the textile dyeing and finishing processes.<sup>2</sup> These pollutants are not only harmful to environment but also hazardous to human health. The adversity of dyes even at trace level attracts the environmentalist and scientist to develop suitable processes for their control. The best alternatives are adsorption as well as photocatalysis because of cost-effectiveness, non-toxic, eco-friendly, reproducibility.3-18 Solar light-driven photocatalysis is a quick and vital process for degradation of organic dyes. Mostly, semiconducting oxides such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, CdSe, ZrO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, etc. have been used as photocatalysts.<sup>6,8,19-22</sup> These semiconducting oxides modified with other metals and oxides are also active for photocatalytic dye degradation, in which dyes are excited by absorbing light photons (sunlight or UV light) and immediately inject electrons into the conduction band (CB) of semiconductor leads initiating the dye degradation.<sup>1</sup> Likewise in the adsorption process, the adsorption of dye occurs efficiently if the adsorbent is highly porous (mesoporous) and contains a high surface area.<sup>23-27</sup> Mainly, mesoporous silica (MCM-41), mesoporous Al<sub>2</sub>O<sub>3</sub> and mesoporous carbon are treated as promising and efficient adsorbents for dye adsorption because of its high surface area and mesoporosity.<sup>28-35</sup>

Although both semiconducting and mesoporous materials show efficient photocatalytic and adsorption activity towards dye removal, but still there are some gaps in photocatalysis and adsorption study. Firstly, in photocatalytic dye degradation, though it is an effective process and degrades organic dyes quickly, it fails to degrade highly concentrated and huge amount of dyes quickly. This is because of the low surface area of semiconducting materials which gives less interaction of dye molecules with catalyst surfaces and decreases the photocatalyst activity. Secondly, in adsorption process, though the high concentrated and huge amount of dye molecule adsorbed onto the mesoporous surface, but it takes more time as compared to photocatalysis. Another problem lies with the disposal of organic dyes after it gets adsorbed onto the adsorbent surface.

In order to avoid these problems, researchers and environmental scientists are in search of alternative materials which can behave both as photocatalysts as well as adsorbents. That means we have to develop a single material which has semiconducting as well as high mesoporous surface property. Hence both photocatalysis as well as adsorption occur simultaneously on this material. In this

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contest, we have developed a mesoporous Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 composite. The mesoporous support Al<sub>2</sub>O<sub>3</sub>-MCM-41 has unique properties such as extremely high surface area (1045 m<sup>2</sup> g<sup>-1</sup>), narrow pore diameter (2.6 nm) and high pore volume (1.64 cm<sup>3</sup> g<sup>-1</sup>), characteristics of an efficient adsorbent. This also gives a platform for Cu impregnation to form mesoporous Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. After 5 wt% of Cu impregnation, the textural properties do not change appreciably: 786 m<sup>2</sup> g<sup>-1</sup> surface area, 2.5 nm pore diameter and 1.34 cm<sup>3</sup> g<sup>-1</sup> pore volume. The most important thing is that after Cu impregnation, the Cu<sup>2+</sup> oxidation state doesn't change, proving the stability of support Al<sub>2</sub>O<sub>3</sub>-MCM-41. Interestingly, it has been reported that metal ions such as Ag<sup>+</sup>, Cu<sup>2+</sup>, Cr<sup>6+</sup>, Hg<sup>2+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> have been used to increase the photocatalytic activity of TiO2.36-38 Few studies have reported that the simultaneous photocatalytic synergistic degradation of dyes and organic compounds accelerates with the reduction of metal ions.<sup>39,40</sup> In our case, the irradiation of sunlight on the surface of mesoporous Cu<sup>2+</sup>/Al<sub>2</sub>O<sub>3</sub>-MCM-41 ejects an electron from the catalyst surface. This process reduces Cu 2+ to Cu+, simultaneously producing holes which generates 'OH radicals and helps to degrade organic dyes. Though Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41is not a semiconducting material like TiO<sub>2</sub>, it is a UV-Vis active material, which leads it to behave as a semiconducting-like material and becomes a visible light responding photocatalyst. It has been reported that at alkaline pH the generation of 'OH radicals is more rapid than at acidic pH.41,42 When Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 reacts with dyes in the basic aqueous medium, it generates a large number of hydroxyl radicals, leading to degradation of the dye molecules. Lastly, the intra-particle mesoporosity enhances the textural properties, resulting in a high amount of dye adsorption on the surface of Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. Moreover, the photocatalytic cationic dye degradation is enhanced via the adsorption process because if there is more adsorption then there will be more interaction of dye molecule and adsorbent, resulting in efficient dye degradation.

Herein, we report the synthesis of high surface area mesoporous  $Cu/Al_2O_3$ -MCM-41, mesoporous  $Al_2O_3$  (MA) and their effective use as efficient photocatalysts and adsorbents for removal of dyes. MA prepared using starch as template was introduced into the framework of MCM-41 (*in situ* synthesis), followed by impregnating different wt% Cu to produce Cu/Al\_2O\_3-MCM41. The extraordinary behaviour of the composite material towards cationic dyes and mixed dyes (MB+MV+MG+Rd 6G) degradation/adsorption was interpreted due to intra-particle mesoporosity, electron transfer and generation of 'OH free radicals.

## Experimental

Mesoporous Al<sub>2</sub>O<sub>3</sub> (MA) was prepared using starch as template. At first 20.2 g of starch was dissolved in minimum amount of deionized water. Then 10.2 g of aluminium isopropoxide was added and stirred vigorously for 30 min at room temperature. The pH of the solution was maintained at 6 and then the solution was kept standing for 5 h. In static condition, complete hydrolysis of aluminium propoxide occurred and resulted in high texture mesoporous Al<sub>2</sub>O<sub>3</sub>. Finally, the mixture was dried at 100 °C in order to remove the volatile impurities. The resultant solid was calcined at 600 °C for 6 h for complete removal of the template. The mesoporous Al<sub>2</sub>O<sub>3</sub>–MCM-41 composite was synthesized by incorporating MA into the MCM-41 during the synthesis (*in situ*). In Al<sub>2</sub>O<sub>3</sub>–MCM-41, the Si/Al ratio was kept 10. The preparation method by Terres *et al.*<sup>43</sup> was adopted here to prepare MCM-41. Different wt% copper such as 5, 10, 15 and 25 was introduced onto Al<sub>2</sub>O<sub>3</sub>–MCM-41 by wetness impregnation method by taking cupric nitrate [(Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) Merck, 98%] as the source of copper. The copper incorporated mesoporous support Al<sub>2</sub>O<sub>3</sub>– MCM-41 named as X Al<sub>2</sub>O<sub>3</sub>–MCM-41, where X is different wt% of copper (5, 10, 15 and 25). Copper-incorporated composite materials were calcined at 600 °C for 6 h. The composites are 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41, 10 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41, 15 Cu/Al<sub>2</sub>O<sub>3</sub>– MCM-41 and 25 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41.

### Characterization

The structure and phase identification were performed by low angle X-ray diffraction (LXRD, Ragaku Miniflex, Cu-Ka radiation). High angle pattern XRD was taken by Philips PANalytical PW 3040/60 instrument using Mo-Kα radiation. N<sub>2</sub> adsorptiondesorption isotherms were measured at 77 K on an ASAP-2020 system from which the surface area (BET), the pore size (BJH), and pore volume were calculated. The transmission electron microscopy images were recorded using FEI, TECNAI G<sup>2</sup> 20, TWIN and the images were recorded by using a Gatan CCD camera. The electronic states were investigated by X-ray photoelectron spectroscopy [XPS, Kratos Axis 165 with a dual anode (Mg and Al) apparatus] using the Mg KR source. FTIR spectra of the samples were recorded in a Varian FTIR spectrophotometer (FTS-800), taking KBr as reference. The optical absorbance spectra was recorded in a UV-vis spectrometer (Shimadzu), using boric acid as the standard.

### Procedure for photocatalytic and adsorption study

The methylene blue (MB), methyl violet (MV), malachite green (MG) and rhodamine 6G (Rd 6G) are used in this work are from Merck, India. A stock solution of each dye (1000 mg  $L^{-1}$ ) was prepared and suitably diluted to the required concentration. Photocatalytic degradation of dyes was carried out by taking 20 ml of MB, MV, MG and Rd (500 mg L<sup>-1</sup>), 1.0 g L<sup>-1</sup> of adsorbent dose at pH 11 in a tightly fitted conical flask. The pH of the solution was adjusted using 0.01 M HNO<sub>3</sub> and/or 0.01 M NH<sub>4</sub>OH (Merck, GR). The pH measurement was carried out with an Elico digital pH meter (model L1-612) using a combined electrodes (model CL 51B). The suspension was stirred by a magnetic stirrer in the presence of sunlight for only 30 min, then centrifuged and the dye concentration was measured using Varian Cary IE UVvisible spectrophotometer (Model EL 96043181) at a wavelength corresponding to the maximum absorbance, 664 nm (MB), 584 nm (MV), 618 nm (MG) and 566 nm (Rd 6G). Likewise, the adsorption experiment was carried out in dark for 60 min and the reaction condition was maintained same as that of photocatalytic experiment (adsorbent dose, pH and dyes concentration). For TOC (Total Organic Carbon) analysis, the centrifuged solution from adsorption and photocatalytic degradation experiment was injected in a TOC analyzer (ANATOC).

### **Results and discussion**

### X-Ray powder diffraction

The low angle XRD pattern of MCM-41, Al<sub>2</sub>O<sub>3</sub>-MCM-41 and 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 are shown in the Fig. 1(a), (b) and (c), respectively. They displayed a strong diffraction peak  $(d_{100})$  along with small and broad signals  $(d_{110} \text{ and } d_{200})$  in the low angle region. This pattern indicated the existence of a hexagonal order in the intra-particle mesoporous system. The XRD patterns of the samples differ only in the peak intensities which are significantly reduced from MCM-41 to 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. The intensities decreased strongly because of incorporation of MA into MCM-41 (Al<sub>2</sub>O<sub>3</sub>-MCM-41) and Cu onto the surface of Al<sub>2</sub>O<sub>3</sub>-MCM-41(5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41). The intensity loss must be attributed to a progressive phase cancellation phenomenon associated with the incorporation of scattering materials into the mesopores.44 This phenomenon takes place when MA incorporated into the MCM-41 (Al<sub>2</sub>O<sub>3</sub>-MCM-41), resulted increase in surface area of Al<sub>2</sub>O<sub>3</sub>-MCM-41 as compared to MCM-41. This indicates that phase cancellation and creation of extra mesopores within the limited phase leads to increase the surface area of Al<sub>2</sub>O<sub>3</sub>-MCM-41. Hence, incorporation of MA into the mesopores MCM-41 gave high surface area Al<sub>2</sub>O<sub>3</sub>-MCM-41 (Table 1). Contrary to it, the incorporation of Cu onto the surface of Al<sub>2</sub>O<sub>3</sub>-MCM-4 led to decrease the surface area of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. This is perhaps due to blockage of mesopores of Al<sub>2</sub>O<sub>3</sub>-MCM-41.



Fig. 1 Low angle XRD patterns for the samples (a) MCM-41, (b)  $Al_2O_3$ -MCM-41, (c) 5 Cu/Al\_2O\_3-MCM-41 and inset high angle XRD pattern of  $Al_2O_3$ -MCM-41 and 5 Cu/Al\_2O\_3-MCM-41.

Additionally, 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 sample exhibits characteristic peaks for CuO crystalline phases whereas  $Al_2O_3$ –MCM-41 is found to be amorphous in absence of any peak in the XRD

Table 1 Textural property of MA, MCM-41,  $Al_2O_3$ -MCM-41 and copper incorporated mesoporous supports

Samples	Si/Al	Surface area $(m^2 g^{-1})$	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore diameter (nm)
MA		250	0.350	7.5
MCM-41		878	0.6599	2.5
Al <sub>2</sub> O <sub>3</sub> –MCM-41	10	1045	1.64	2.6
$5  \text{Cu/Al}_2\text{O}_3 - \text{MCM-41}$	10	786	1.34	2.5
10 Cu/Al <sub>2</sub> O <sub>3</sub> -MCM-41	10	564	0.560	2.3
15 Cu/Al <sub>2</sub> O <sub>3</sub> -MCM-41	10	515	0.481	2.4
25 Cu/Al <sub>2</sub> O <sub>3</sub> -MCM-41	10	380	0.393	2.2

pattern (inset in Fig. 1). The crystal size of Cu(II) particles in  $Al_2O_3$ -MCM-41 was calculated from the Scherrer equation.

$$L = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where L is the crystallite size (Å),  $\lambda$  the wavelength (Å),  $\beta$  is the line broadening at half the maximum intensity in radians and the  $\theta$  the angle of the highest peak in radians. The crystallite size of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 was found to be 38 nm.

#### N<sub>2</sub> adsorption-desorption isotherm

The N<sub>2</sub> adsorption-desorption isotherm and pore size distribution of MCM-41, Al<sub>2</sub>O<sub>3</sub>–MCM-41, 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 and MA are shown in the Fig. 2 and Fig. 3, respectively. The textural properties such as BET surface area, pore diameter and pore volume derived from the N<sub>2</sub> adsorption-desorption measurements are included in Table 1. N<sub>2</sub> sorption resulted typical type IV isotherm which is defined by Brunaure *et al.*<sup>45</sup> It indicated that all the samples are mesoporous in nature. Moreover, a steeper N<sub>2</sub> adsorption step in the mid-relative pressure range of 0.1 to 0.8 is indicative of relatively intra particle mesoporosity, which is shown in the Fig. 2. The pore size distribution curves (Fig. 3) of all materials are mono modal showing that they belong to narrow mesoporous range in between 2–3 nm (except MA 7.5 nm),



Fig. 2  $N_2$  adsorption-desorption isotherm of MCM-41,  $Al_2O_3$ -MCM-41,5 Cu/Al\_2O\_3-MCM-41 and MA.



Fig. 3 Pore size distributions of (a)  $Al_2O_3$ -MCM-41, (b) MCM-41, (c) 5 Cu/Al\_2O\_3- MCM-41 and (d) MA.

indicating that the presence of intra-particle mesoporosity which is consistent in the BET pore size measurement (Table 1).

The textural properties, such as surface area, pore diameter and pore volume of samples, were measured using BET method by N<sub>2</sub> adsorption-desorption, and are shown in Table 1. The pore diameter of MCM-41, Al<sub>2</sub>O<sub>3</sub>-MCM-41 and Cu-doped Al<sub>2</sub>O<sub>3</sub>-MCM-41 shows narrow pore diameter within 2-3 nm (mesoporous), indicating the presence of intra-particle mesoporosity. The high specific surface area of Al<sub>2</sub>O<sub>3</sub>-MCM-41 compared to MCM-41 indicated that the incorporation of mesoporous Al<sub>2</sub>O<sub>3</sub> (MA) into the MCM-41 framework. That means after incorporation of MA, Si(IV) atom of MCM-41 was replaced by Al(III) and also Al(III) coordinate to Si(IV) gives extra-framework Al<sub>2</sub>O<sub>3</sub>-MCM-41. After Cu incorporation onto the surface of Al<sub>2</sub>O<sub>3</sub>-MCM-41, the Cu(II) covers the surface of Al<sub>2</sub>O<sub>3</sub>-MCM-41, resulting in blocking of mesopores, leads to a decrease in the surface area from 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41to 25Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. The high pore volume of Al<sub>2</sub>O<sub>3</sub>-MCM-41 indicated that incorporation of MA does not affect the pore structure of MCM-41 framework, rather extends orderliness as well as intra-particle mesoporosity. This is because Al(III) substitutes Si(IV), leading to formation of extraframework Al<sub>2</sub>O<sub>3</sub>-MCM-41. Lastly, MA shows high surface area, pore volume and pore diameter due to the micellar formation of starch and the slow hydrolysis of aluminium isopropoxide, leading to the development of the textural property of MA.

### **TEM** analysis

TEM analysis (Fig. 4) was performed to examine the size, shape and orientation of mesoporous Al<sub>2</sub>O<sub>3</sub>-MCM-41 and Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. Fig. 4(a) shows the TEM image of mesoporous Al<sub>2</sub>O<sub>3</sub>-MCM-41. The particles are well separated and porous in nature. The intergrowth of MA into the framework of MCM-41 led to extra framework in Al<sub>2</sub>O<sub>3</sub>-MCM-41, resulted in an intra-particle mesoporous (small pores) structure. However, the low angle XRD, N<sub>2</sub> adsorption-desorption isotherm and narrow pore size from BET measurement also agreed the intra-particle mesoporosity of Al<sub>2</sub>O<sub>3</sub>-MCM-41. Not merely Al<sub>2</sub>O<sub>3</sub>-MCM-41 but also 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 showed intra-particle mesoporous structure (Fig. 4(b)). That means Cu incorporation onto the surface of Al<sub>2</sub>O<sub>3</sub>-MCM-41 did not affect the intra-particle mesoporosity but affected the order of the particles, resulting in a decrease in the surface area of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 as compared to Al<sub>2</sub>O<sub>3</sub>-MCM-41 (Table 1). Moreover, the particle size of 5  $Cu/Al_2O_{3-}$ 

# MCM-41was 36 nm (calculated from Fig. 4(b)), which was nearly similar with the crystallite size obtained by the Scherrer equation.

### XPS study

The XPS study of mesoporous composite Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 depicts the electronic environment and oxidation state of Cu, Al and Si. The XPS band of Cu 2p, Si 2p, Al 2p and O 1s core levels are shown in Fig. 5(a), (b), (c) and (d), respectively. The binding energy of Si 2p in pristine SiO<sub>2</sub> and Al 2p in Al<sub>2</sub>O<sub>3</sub> is 103.5 and 75 eV, respectively.46,47 But when MA incorporated into framework of MCM-41 (Al<sub>2</sub>O<sub>3</sub>-MCM-41) and Cu immobilised onto the surface of Al<sub>2</sub>O<sub>3</sub>-MCM-41 the binding energy of Si 2p became 104.1 eV. The shifting of BEs of Si 2p towards higher value might be due to the strong interaction between Al<sup>3+</sup> and Si<sup>4+</sup> through oxygen atom. The higher shift of BEs for Si 2p and lower shift for Al<sup>3+</sup> (74.55 eV) might be due to the transfer of electrons from Si<sup>4+</sup> to Al<sup>3+</sup> and also suggesting some Si<sup>4+</sup> atom is replaced by Al<sup>3+</sup>. Thereby, it is concluded that mesoporous Al<sub>2</sub>O<sub>3</sub>-MCM-41 consisted of Al-O-Si network. The present study showed that the binding energies (BEs) of Cu  $2p_{3/2}$  and Al  $2p_{3/2}$  were found to be at 933.55 eV and 74.55 eV, suggesting the presence of Cu in 2+ oxidation state and Al in 3+ oxidation state. It has been reported that the binding energy of Cu<sup>2+</sup> is 933 eV.<sup>48–49</sup> The BEs of Cu 2p<sub>3/2</sub> shifted towards higher values and the Al 2p<sub>3/2</sub> towards lower values indicated a strong metal-support interaction. The electronic interaction might be due to transfer of electron from Cu<sup>2+</sup> to Al<sup>3+</sup>. As a result Cu bonded with aluminium to form a Cu-Al network. Thus, 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 consisted of Cu-Al-O-Si linkage. The BE of O 1s was 532.45 eV, which might be due to close interaction of oxygen atom with Si compared to Al atoms.

### **UV-VIS DRS spectra**

The UV-vis diffuse reflectance spectra of Al<sub>2</sub>O<sub>3</sub>-MCM-41 and different wt% of Cu impregnated Al<sub>2</sub>O<sub>3</sub>-MCM-41 samples are shown in Fig. 6. All the catalysts showed a very strong absorption band at 260 nm, which is due to the ligand to metal charge transfer (LMCT) between surface oxygen and isolated Cu<sup>2+</sup> ions.<sup>50</sup> It has been observed that the spectra which is situated both visible and near-IR, predicating potential photocatalytic activity.51 In Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41, the d-d transition band for octahedrally coordinated Cu2+ species was observed at 760 nm,52 which is in between visible and near IR, indicating the photocatalytic activity. This peak is absent in Al<sub>2</sub>O<sub>3</sub>-MCM-41, indicating less photocatalytic activity than Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. If the copper content is increased, the charge transfer band of Cu ions become broader, showing an additional spectra in between 310-360 nm, indicated the formation of small amount of Cu clusters in a highly dispersed state (Shimokawabe et al.).53

### FTIR spectra

The FTIR spectra of solid MB, MV, MG, Rd 6G and  $5 \text{ Cu/Al}_2\text{O}_3$ – MCM-41 before and after photocatalytic reaction of mixed dyes are shown in the Fig. 7(a), (b), (c), (d), (e) and (f), respectively. Mainly, the spectra at 1603 cm<sup>-1</sup> and 1394 cm<sup>-1</sup> are due to the presence of aromatic ring of pure MB.<sup>54</sup> The spectra at 1584 cm<sup>-1</sup> and 1366 cm<sup>-1</sup> are assigned to N–H bending vibration

Fig. 4 Representative TEM micrographs for samples (a)  $Al_2O_3$ -MCM-41 and (b) 5 Cu/Al\_2O\_3-MCM-41.





Fig. 5 XPS of spectrum of 5  $Cu/Al_2O_3$ -MCM-41 Cu 2p core-level spectrum, (b) Si 2p spectrum, (c) representative Al 2p spectrum and (d) O 1s core level.



Fig. 6 UV-Vis absorption spectra of 5, 10, 15 and 25 wt% of Cu/Al\_2O\_3–MCM-41 and Al\_2O\_3–MCM-41.

and conjugated double bond of pristine MV. For pure MG, the N–H bending vibration and conjugated double bond occurred at 1596 and 1366 cm<sup>-1</sup>, respectively.<sup>55</sup> In Rd 6G, the spectra at 3265 cm<sup>-1</sup> is due to the stretching frequency of  $-NH_2$  group. The band at 1612 and 1323 cm<sup>-1</sup> are due to the stretching vibration of C=O and C–O, respectively.<sup>56</sup> Fig. 7(e) shows the FTIR spectra of 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41, the spectra at 960 cm<sup>-1</sup> is due to Al–O–Si and Si–O–OH. The band 1078 cm<sup>-1</sup> corresponds to the asymmetric stretching vibration mode of bond Si–O–Si. A very broad peak at 1627 cm<sup>-1</sup> is due to -OH group. The shoulder peak at 580 cm<sup>-1</sup> corresponds to the Cu–O stretching modes.<sup>57</sup>



Fig. 7 FTIR spectra of (a) MB, (b) MV, (c) MG, (d) Rd 6G, (e) 5  $Cu/Al_2O_3$ -MCM-41 and (f) after mixed dyes degradation on the surface of 5Cu/Al\_2O\_3-MCM-41.

Fig. 7(f) shows the spectra of 5  $Cu/Al_2O_3$ –MCM-41 after mixed dye degradation. That means after mixed dye degradation, the collected samples dried in air and IR spectra was taken in order to know whether the mixed dyes are adsorbed or degrade on the surface of 5 Cu/Al\_2O\_3–MCM-41. But surprisingly it was observed

that the spectra of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 (after degradation), showed exactly similar spectra as that of pristine 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 (Fig. 7(e)). These results clearly indicate that the dye molecules are adsorbed on the surface of photocatalyst and then degraded completely. If dye molecules are adsorbed on the catalyst surface then spectra of different dyes will come after adsorption. The absence of different dyes spectra after degradation indicated that adsorption is not an optimum process for removal of mixed dyes. The other factor is photocatalytic decomposition of mixed dyes in presence of sunlight and catalyst, leading to degradation of mixed dyes. In this result, we also confirmed that the electron transfer and generation of 'OH radical took place which helped photocatalytic degradation of mixed dyes. Hence, the photocatalytic process of mixed dye degradation is predominant over the adsorption process. Conclusively, in mixed dyes, dye molecules are adsorbed on the surface of the 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 then degraded completely in presence of sunlight within 30 min.

### Effect of pH

The pH is the most important factor affecting the adsorption process. The adsorption process was performed in dark at room temperature taking high concentrated dye solution such as Rd 6G of 500 mg L<sup>-1</sup>, 1g L<sup>-1</sup> adsorbent and 60 min reaction time. Fig. 8 depicts the adsorption proficiency of Rd 6G with different types of adsorbents at various pH (3, 5, 7, 9 and 11). 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41showed highest adsorption efficiency as compared to other mentioned adsorbents. Even high surface area adsorbent, Al<sub>2</sub>O<sub>3</sub>-MCM-41 failed to compete with 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41, though adsorption is a surface phenomenon. The synergistic effect of copper with mesoporous support Al<sub>2</sub>O<sub>3</sub>-MCM-41 (metal-support synergistic effect) is responsible for high Rd 6G adsorption on the surface of 5 Cu/AM 10. That means lower amount of Cu enhances the active sites, resulted high percentage of adsorption. The adsorption efficiency gradually decreases from 10 to 25 wt% Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41%. High percentage of copper incorporation



**Fig. 8** Effect of pH on the percentage of RD 6G adsorption on different type of investigated adsorbents. The pH varied from 3 to 11. The reaction was proceeded by taking 1.0 g  $L^{-1}$  of adsorbent, 500 mg  $L^{-1}$  of RD 6G. The reaction was carried out in absence of sunlight and room temperature for 60 min.

**Table 2** Adsorption percentage of different dyes such as MB, MV, MG and Rd 6G by different adsorbents. The adsorption processes were carried out 20 ml of 500 mg  $L^{-1}$  dyes concentration, pH 11, reaction time 60 min at dark and the adsorbent dose was 1g  $L^{-1}$ 

	Adsorption (%)					
Adsorbent	MB	MV	MG	Rd 6G		
m-Al <sub>2</sub> O <sub>3</sub>	34	48	54	78		
MCM-41	44	58	65	83		
Al <sub>2</sub> O <sub>3</sub> -MCM-41	84	94	93	95		
$5 Cu/Al_2O_3-MCM-41$	91	99	98	99		
$10 \text{ Cu/Al}_{2}\text{O}_{2}-\text{MCM-41}$	68	88	92	96		
$15 \text{ Cu/Al}_{2}\text{O}_{2}-\text{MCM-41}$	60	85	90	93		
25 Cu/Al <sub>2</sub> O <sub>3</sub> -MCM-41	55	80	87	88		

led to pore blocking of adsorbent surface. Another factor is that in high copper loading, there is the possibility that one copper ion sat over another copper ion, decreasing the active sites, resulted less adsorption. The adsorption efficiency of Al<sub>2</sub>O<sub>3</sub>-MCM-41 is higher than the pure MCM-41 and MA. This is because of high surface area, intra-particle mesoporosity and combined effect of Al<sub>2</sub>O<sub>3</sub> and MCM-41. As 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 showed high adsorption, so the pH study emphasized only by using 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 as the adsorbent. It was observed that the Rd 6G adsorption percentage increases with increases in pH, 100% adsorption occurred within 60 min at pH 11, shown in Fig. 8. This can be explained on the basis of  $pH_{pzc}$  of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. The pH<sub>pzc</sub> of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 is 2.3. Thus, it seems likely that, for pH values above 2.3, there is negatively charged density on the surface of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. Acid medium (pH 2.3) is unfavourable for the association of the cationic adsorbate Rd 6G because of electrostatic repulsion. Hence, the pH above 2.3 surface charged becomes negative, at pH 11 becomes more negative which gives platform for adsorption of Rd 6G very quickly through electrostatic interaction. Not only Rd 6G, the other cationic dyes such as MB, MV and MG also gave high adsorption property which is shown in the Table 2. Our main focus is photocatalytic degradation of cationic dyes in the presence of sunlight. By keeping this knowledge, we have proceeded with degradation experiments of photocatalytic dyes (MB, MV, MG and Rd 6G) at pH 11.

#### Photocatalytic dyes degradation

Photocatalytic degradation of MB, MV, MG and Rd 6G over different catalysts were investigated over 5Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 and Al<sub>2</sub>O<sub>3</sub>-MCM-41. The reaction was carried out by taking single dye (not mixed) in the presence of sunlight, pH 11, 1g L<sup>-1</sup> catalyst dose, 500 mg L<sup>-1</sup> dye concentration and 30 min reaction duration. Table 3 showed that nearly 100% dye degradation took place on 5Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. Mainly, three factors are responsible for quick dye degradation on 5Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41. These are intraparticle mesoporosity, electron transfer and generation of 'OH radicals. The 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41 sample showed high surface area because of intra-particle mesoporosity. The high surface area gave wide space for excited dye molecules to adsorb onto it. As the surface area is more, the whole dye molecules adsorbed immediately and reaction took place between dye molecules and catalyst surface in the presence of sunlight. After light absorption, the photoelectrons (e<sup>-</sup>) in the valence band (VB) excited to the conduction band (CB) causing the generation of holes (h<sup>+</sup>) in

**Table 3** Photocatalytic dye (MB, MV, MG and Rd 6G) degradation and TOC removal using present investigated catalyst. The reaction was carried out in presence of sunlight, pH 11, 500 mg  $L^{-1}$  of dyes concentration, 1g  $L^{-1}$  of catalyst and the reaction time was only 30 min

Catalyst	Degradation (%)				TOC removal (%)			
	MB	MV	MG	Rd 6G	MB	MV	MG	Rd 6G
MA	50	65	68	77	22	28	30	33
MCM-41	55	67	69	79	23	29	31	34
Al <sub>2</sub> O <sub>3</sub> -MCM-41	81	83	85	93	38	39	39	41
$5 Cu/Al_2O_3-MCM-41$	100	98	99	100	80	85	78	89
$10 \text{ Cu/Al}_{2}\text{O}_{3}-\text{MCM-41}$	70	88	89	94	55	62	65	71
$15 \text{ Cu/Al}_{2}\text{O}_{3}-\text{MCM-41}$	64	79	84	92	45	51	57	69
$25 \text{ Cu/Al}_2\text{O}_3$ -MCM-41	60	72	76	84	49	52	55	65



Scheme 1 Technological and mechanistic pathways for dye degradation on the surface of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41.

the VB simultaneously. A portion of the electrons reduced Cu<sup>2+</sup> to Cu<sup>+</sup> ion, it thereby acting as an electron scavenger. Hence, electron-hole recombination was prevented, shown in Scheme 1 (Mechanism-1). The resultant holes h<sup>+</sup> in the VB reacted with OH<sup>-</sup> to produce 'OH. The other portion of electrons transferred to the surface and reacted with the ubiquitously oxygen molecule to yield 'O<sub>2</sub>. The generated 'O<sub>2</sub> further combined with H<sup>+</sup> to produce 'HO<sub>2</sub>. When 'HO<sub>2</sub> radical combined with other 'HO<sub>2</sub>, formed H<sub>2</sub>O<sub>2</sub>. The 'OH radicals could be generated when a H<sub>2</sub>O<sub>2</sub> molecule captured a trapped electron. The reactive species, such as 'OH, 'HO<sub>2</sub>, and h<sub>VB</sub><sup>+</sup>, could all oxidize cationic dyes like MB, MV, MG and Rd 6G in some degree; all steps are shown in Scheme 1 (Mechanism-1).

It has been observed by Rader *et al.* and Dutta *et al.*<sup>41,42</sup> that highly alkaline medium is suitable for generation of 'OH. As the generated hydroxyl radicals ('OH) played a key role in the degradation of dyes, the present MB, MV, MG and Rd 6G degradation experiment was performed over 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 at pH 11 (highly alkaline). Obviously, the alkaline pH is suitable for generation of 'OH radicals, hence degrades the cationic dyes very quickly. The generated 'OH radical oxidized the dye molecules and also produced 'OH *via* generating 'O<sub>2</sub>, 'HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> which are shown in Scheme 1 (Mechanism-2).

In order to check which factor is responsible for dye degradation, we have performed three types of reaction by mixing equal amounts of four dyes (mixed dyes). In type-1, experiment was performed in the absence of light at pH 3.4 (mixed dyes pH).

It was observed that only 20% of mixed dyes adsorbed on the surface of 5 Cu/Al<sub>2</sub>O<sub>3</sub>-MCM-41, showed by negligible colour changed in Fig. 9. Hence, intra-particle mesoporosity and surface area has a marginal effect for mixed dye adsorption/degradation. In type-2, the reaction was carried out in the absence of sunlight at pH 11, the mixed dyes adsorption/degradation percentage was 63 and the colour also changed (Fig. 9). This indicates that intra-particle mesoporosity/high surface area and generation of 'OH in alkaline medium are responsible for enhancement mixed dye adsorption/degradation. Moreover, in type-3, the mixed dyes degradation process was carried out in the presence of sunlight at pH 11; the colour of the solution completely changed as shown in Fig. 9 and percentage of dyes degradation was 94%, indicating that three factors, intra-particle mesoporosity, electron transfer and generation of 'OH radicals, are responsible for a high percentage of dye degradation. Conclusively, individual effect such as intraparticle mesoporosity, electron transfer and 'OH radicals generation are not responsible for mixed dyes degradation. The combined effects of the above three are responsible for high concentrated dyes degradation which led to degradation of mixed dyes within 30 min. The dye degradation activity shown by 5  $Cu/Al_2O_3$ -MCM-41was found to be higher in comparison to  $Al_2O_3$ -MCM-41. Although Al<sub>2</sub>O<sub>3</sub>-MCM-41 possessed a high surface area, it showed less dye degradation as well as TOC removal activity. This can be explained on the basis of electron-hole recombination. Photoluminescent (PL) studies have been undertaken to explain the electron-hole recombination characteristics. It is well known Downloaded by University of Sussex on 25 July 2012 Published on 16 June 2011 on http://pubs.rsc.org | doi:10.1039/C1DT10363F that the PL emission results from the recombination of the excited electrons and holes. Hence the lower PL intensity indicates a lower recombination rate.<sup>58</sup> Fig. 10 shows that the PL spectra of  $Al_2O_3$ -MCM-41 and 5 Cu/Al\_2O\_3-MCM-41. It is observed that the PL intensity of 5 Cu/Al\_2O\_3-MCM-41 sample is lower than the  $Al_2O_3$ -MCM-41. This indicated that the recombination of charges decreased after doping of Cu onto the surface of  $Al_2O_3$ -MCM-41. But in case of  $Al_2O_3$ -MCM-41, PL intensity is more, resulted more electron-hole recombination. As a result photocatalytic dye degradation in some extends led to less dye degradation as compared to 5 Cu/Al\_2O\_3-MCM-41.

 Type-1
 Type-2
 Type-3

 Fig. 9
 Type-1 = mixed dyes adsorption/degradation without sunlight

Fig. 9 Type-1 = mixed dyes adsorption/degradation without sunlight at pH 3.5, Type-2 = mixed dyes adsorption/degradation at pH 11 and Type-3 = mixed dyes degradation at pH 11 in presence of sunlight.



Fig. 10 Photoluminescence spectra of  $Al_2O_3\text{-}MCM\text{-}41$  and 5 Cu/  $Al_2O_3\text{-}MCM\text{-}41.$ 

## Conclusions

The mesoporous 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 composites is found to behave just like a semiconducting material and showed excellent activity for photocatalytic dyes degradation in presence of sunlight. The high texture MA has been synthesized using starch as template and incorporated *in situ* into the framework MCM-41. This process forms a high surface area mesoporous support Al<sub>2</sub>O<sub>3</sub>–MCM-41 which converted to 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 by impregnation of copper. The 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 and Al<sub>2</sub>O<sub>3</sub>– MCM-41 showed intra-particle mesoporosity and high textural properties such as high surface area, narrow pore diameter and wide pore volume which gives platform to adsorb MB, MV, MG and Rd 6G. The intra-particle mesoporosity, electron transfer and generation of 'OH are the key properties of 5 Cu/Al<sub>2</sub>O<sub>3</sub>– MCM-41 which aid degradation of highly concentrated 500 mg  $L^{-1}$  dyes within 30 min. 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 is not only an efficient catalyst for single dye degradation process but also treated as an excellent catalyst for mixed dyes degradation. Thus, 5 Cu/Al<sub>2</sub>O<sub>3</sub>–MCM-41 act as an efficient photocatalyst/adsorbent for photocatalytic degradation and adsorption of dyes and will act as a futuristic material to control the industrial pollution.

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