Supplementary material

Fabrication of Nano-Ag Encapsulated on $ZnO/Fe_2V_4O_{13}$ Hybrid-Heterojunction for Photodecomposition of Methyl Orange

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Chemicals used for this study

The commercial azo dyes Methyl Orange (MO) (C.I No-13025) (molecular formula: $C_{14}H_{14}N_3NaO_3S$ and molecular weight: 327.34), zinc nitrate hexahydrate, silver sulfate, ethanol, methanol (HiMedia), oxalic acid, sodium nitrate (Merck), ferric nitrate hexahydrate, ammonium metavanatate (Qualigens), silver nitrate, ammonium ferrous sulfate, mercury sulfate, ferroin, H_2SO_4, dichloromethane (SD Fine-Chem Ltd.) were used as received. The experimental solution was prepared using distilled water. The pH of the solution before irradiation was adjusted using H_2SO_4 or NaOH.

Characterization techniques

Fourier transform-infrared spectra were recorded using Thermo Nicolet iS5 FT-IR spectrometer in KBr pellet. About 5 mg of sample was mixed with 50 mg of IR grade KBr, ground and pressed using hydraulic press under a pressure of 15 tons into a wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range of 4000–400 cm^{-1}. The spectra were recorded as percentage transmittance against wavenumber. X-Ray diffraction spectra were recorded on the Equinox-1000 model X-ray diffractometer from analytical instruments operated at a voltage of 30 kV and a current of 30 mA with CuK_α (1.54056 Å) radiation. Average crystallite size was determined according to the Debye-Scherrer equation. Brunauer-Emmett-Teller method was utilized to calculate the specific surface area of the materials. By using Barrett-Joyner-Halenda (BJH) model, the pore size distribution was derived from the desorption branches of the isotherms at a relative pressure (P/Po) of 0.98. To determine the textural properties of the synthesized materials, N_2 adsorption-desorption measurements were carried out at 77 K using a Micromeritics ASAP 2020 Norcross, GA, USA. SEM images were taken using Carlziess specifications EVO18 scanning electron microscope. Samples were mounted on a carbon platform placed in the scanning electron microscope for taking images at various magnifications. EDX (Bruker-X-Flash × 130) was performed at different points of the surface in order to minimize any possible anomalies arising from the heterogeneous nature of the analyzed surface. The Jeol 2100 high resolution transmission electron microscopy (HR-TEM) were used to examine the morphology of the nanocomposite working at 200 kV with maximum magnification 2000X–1500000X and resolution 0.2 nm.

The HR-TEM samples were prepared by the ultrasonic dispersion of small amount of the powders in a few milliliters of ethanol, and then dropping on a copper grid covered in an amorphous carbon film. The diffuse reflectance spectra of all the catalysts recorded in Shimadzu UV-1650 PC spectrometer using powdered $BaSO_4$ as a reference. A Horiba Jobin Yvon (Model: Fluorolog FL3-111) spectrofluorometer was employed to record the photoluminescence spectra of the samples at room temperature. Ultraviolet and visible light absorbance spectra were measured over a range of 800–200 nm with a Shimadzu UV-1650 PC recording spectrometer using a quartz cell with 1 cm optical path length and the absorption spectra were recorded with a reference to deionized water. The experiments were performed at room temperature. Intermediates formed during degradation were identified by GC-MS analysis of solutions obtained after different irradiation times. GC-MS analysis was carried out using Varian 2000 Thermo with the following features: capillary column VF5MS (5% phenyl – 95% methylpolysiloxane), 30 m length, 0.25 mm internal diameter, 0.25 μm film thickness, temperature of column range from 50–280 °C (10 °C min^{-1}) and injector temperature 250 °C, attached with mass spectrometer model SSQ 7000.

Photocatalytic degradation experiments

In all experiments 50 mL of the dye solution containing appropriate quantity of the catalyst was used. The suspension was stirred for 30 min in dark and then it was irradiated. The solution and dye was continuously aerated by a pump to provide oxygen and for complete mixing of reaction medium. At specific time interval, 2 to 3 mL of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the centrifugate was diluted to 10 mL and its absorbance was measured at max = 464 nm (decolourization), 272 nm (degradation) using UV-vis spectrophotometer to determine the concentration of dye. From the concentration of dye during the degradation process, percentage of dye remaining was determined.

The photocatalytic degradation of MO was obeyed *pseudo*-first order kinetics. At low initial dye concentration the rate expression is given by

$$d[C]/dt = k'[C] \quad \ldots (1)$$

where k' is the *pseudo*-first order rate constant. The dye is adsorbed onto the immobilized catalyst surface and adsorption-desorption equilibrium is reached in 30 min. After adsorption, the equilibrium concentration of the dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integration of eqn. 1 (with the limit of $C = C_0$ at $t = 0$ with C_0 being the equilibrium concentration of the bulk solution) gives eqn. 2

$$\ln (C_0/C) = k't \qquad \ldots (2)$$

where C_0 is the equilibrium concentration of dye and C is the concentration at time t. *Pseudo*-first order rate constant k' was determined from the plot of ln C_0/C *Vs* t.

Chemical oxygen demand (COD) measurements

COD was determined using the following procedure. Sample was refluxed with $HgSO_4$, known volume of standard $K_2Cr_2O_7$, Ag_2SO_4 and H_2SO_4 for two hours and titrated with standard ferrous ammonium sulfate (FAS) using ferroin as indicator. A blank titration was carried out with distilled water instead of dye sample. COD was determined using the following equation

$$\text{COD} = \frac{(\text{Blank titre value} - \text{dye sample titre value}) \times \text{normality of FAS} \times 8 \times 1000}{\text{Volume of sample}}$$

Photoreactor

Heber multilamp photoreactor model HML-MP 88 (Figure S1) was used for photodegradation experiment with UV-A light. This model consists of eight medium pressure mercury vapour lamps of 8 W, set in parallel, emitting 365 nm wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminium and built in cooling fan at the bottom. It is provided with magnetic stirrer at the centre. Open borosilicate glass tube of 50 mL of capacity, 40 cm height and 12.6 mm diameter was used as a reaction vessel with the total radiation exposure length of 330 mm. The irradiation was carried out using four parallel 8 W medium pressure mercury lamps in open-air condition. The light intensity was measured using ferrioxalate actinometer and it is found to be 1.381×10^{-6} einstein L^{-1} s^{-1}.

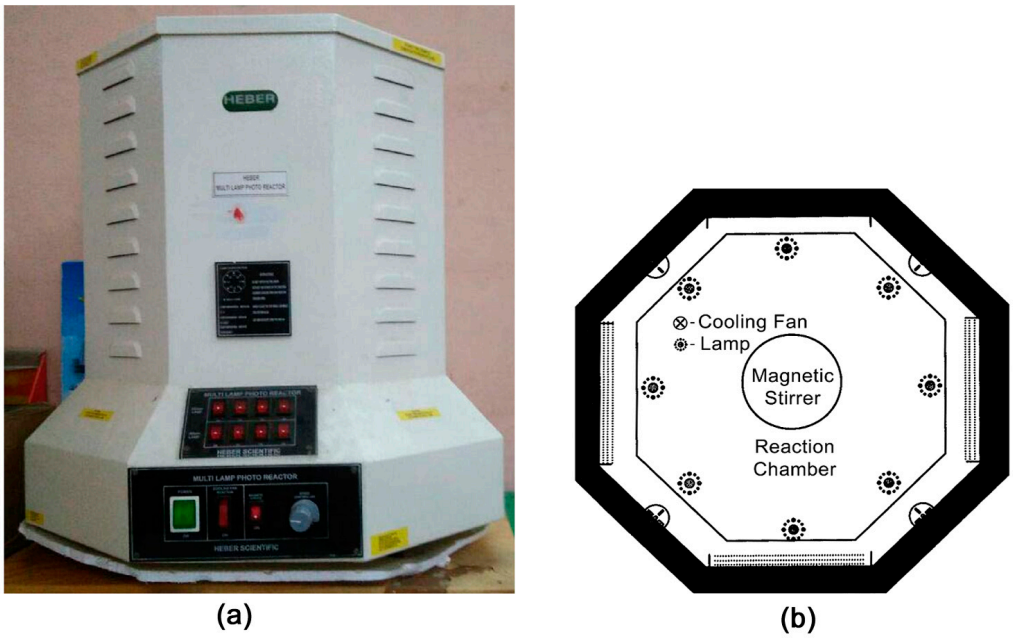

Figure S1 Photoreactor of a) full view and b) top view.

Table S1. Kinetic values in the photodegradation of different process

Process	a	b	c	d	e	f	g
k (min^{-1})	0.0139	0.0264	0.0161	0.0216	0.0010	0.0377	0.0129

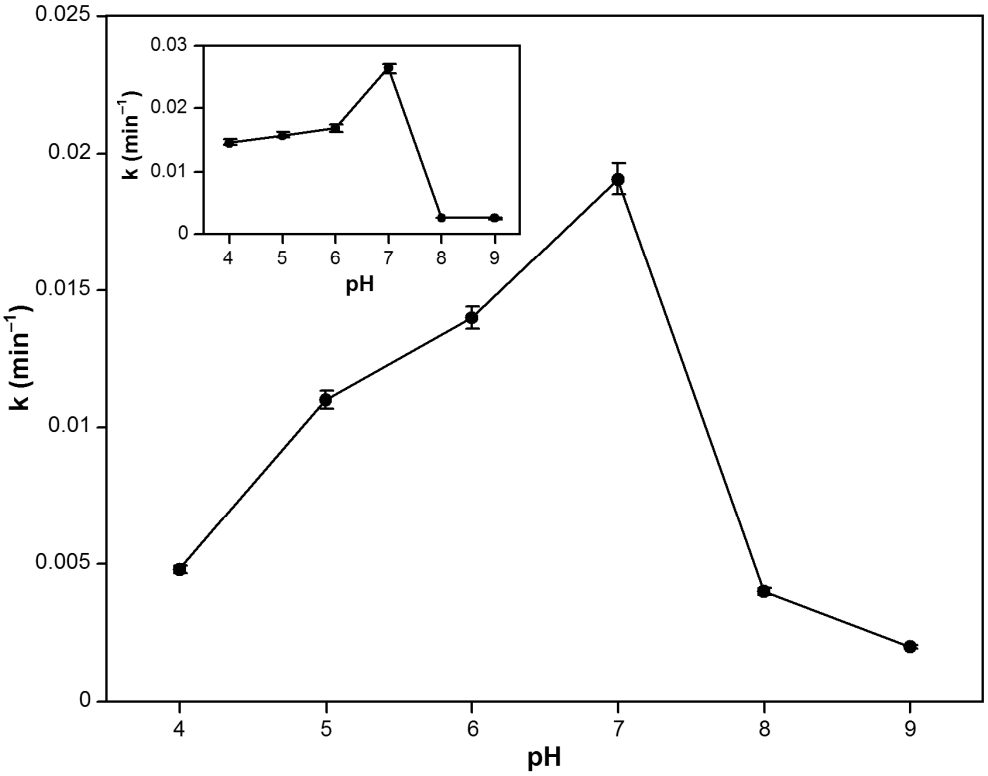

Figure S2 Effect of pH (degradation). [MO] = 4×10^{-4} M, 2 wt% Ag-ZnO/$Fe_2V_4O_{13}$ = 2 g L^{-1}, airflow rate = 8.1 mL s^{-1}, irradiation time = 30 min, I_{UV} = 1.381×10^{-6} einstein L^{-1} s^{-1}. Inset shows effect of pH (decolorization).

Effect of catalyst loading

To avoid the excess use of the catalyst, it is necessary to calculate the optimum dose (or) loading of the catalyst for the efficient removal of dye. The photocatalytic degradation and decolorization of MO with Ag-ZnO/$Fe_2V_4O_{13}$ under UV-A light is shown in Figure S3. It revealed that initially as catalyst loading increased from 1 to 3 g L^{-1}, the degradation (40% to 90%) and decolorization (42% to 99%) efficiency also increased at 60 min, further increase the catalyst loading, there is a decrease in efficiency observed. The maximum percentage of photocatalytic degradation and decolorization is observed at 3 g L^{-1}. Further increase of catalyst amount (above 3 g L^{-1}) decreases the removal efficiency. Enhancement of removal efficiency is due to the following reasons: i) the dosage of catalyst increases the amount of dye adsorbed on the surface of catalyst, ii) the area of illumination may also increase. The decrease in efficiency of MO at higher dosage (above 3 g L^{-1}) may be due to

light scattering effect by the catalyst. The optimum amount of catalyst for efficient degradation of MO is 3 g L^{-1}.

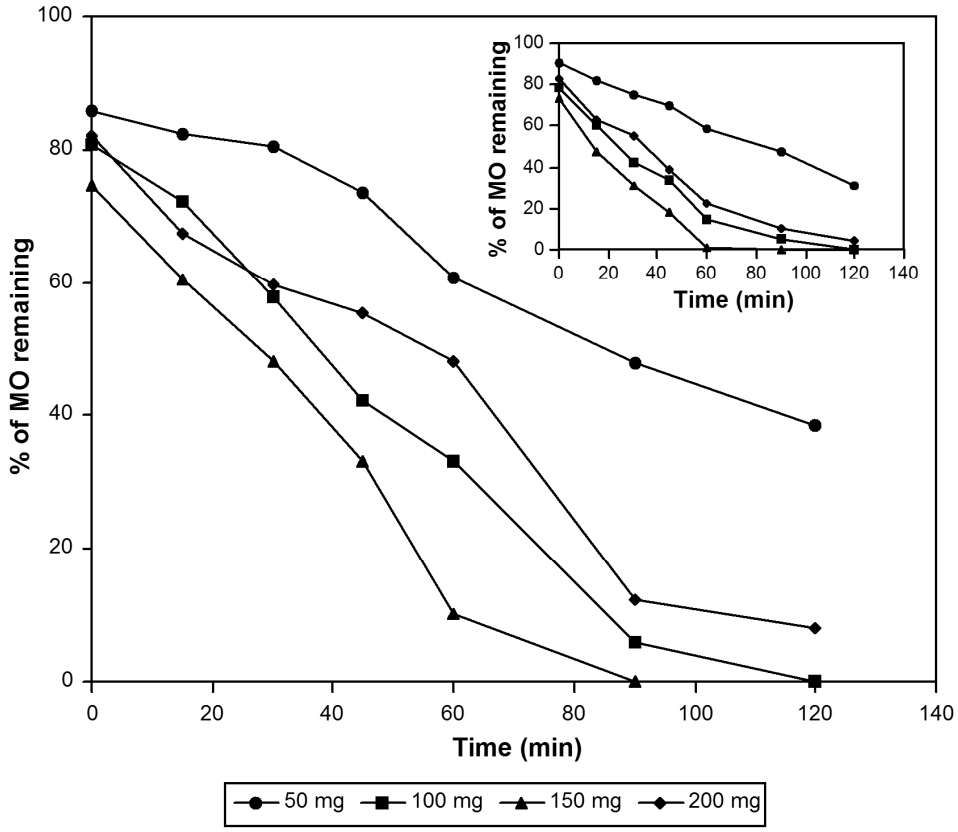

Figure S3 Effect of catalyst loading (degradation). [MO] = 4×10^{-4} M, airflow rate = 8.1 mL s^{-1}, pH = 7.0, I_{UV} = 1.381×10^{-6} einstein L^{-1} s^{-1}. Inset shows effect of catalyst loading (decolorization).

Effect of dye concentration

The photocatalytic degradation and decolorization of the MO were carried out by varying the dye concentrations from 1 to 5×10^{-4} M. The result (Figure S4) showed that the dye concentration influences the degradation and decolorization efficiency. Initially, as the concentration of the dye increased from 1 to 5×10^{-4} M, the photocatalytic degradation (0.045 to 0.014 min^{-1}) and decolorization (0.058 to 0.015 min^{-1}) rate decreased.

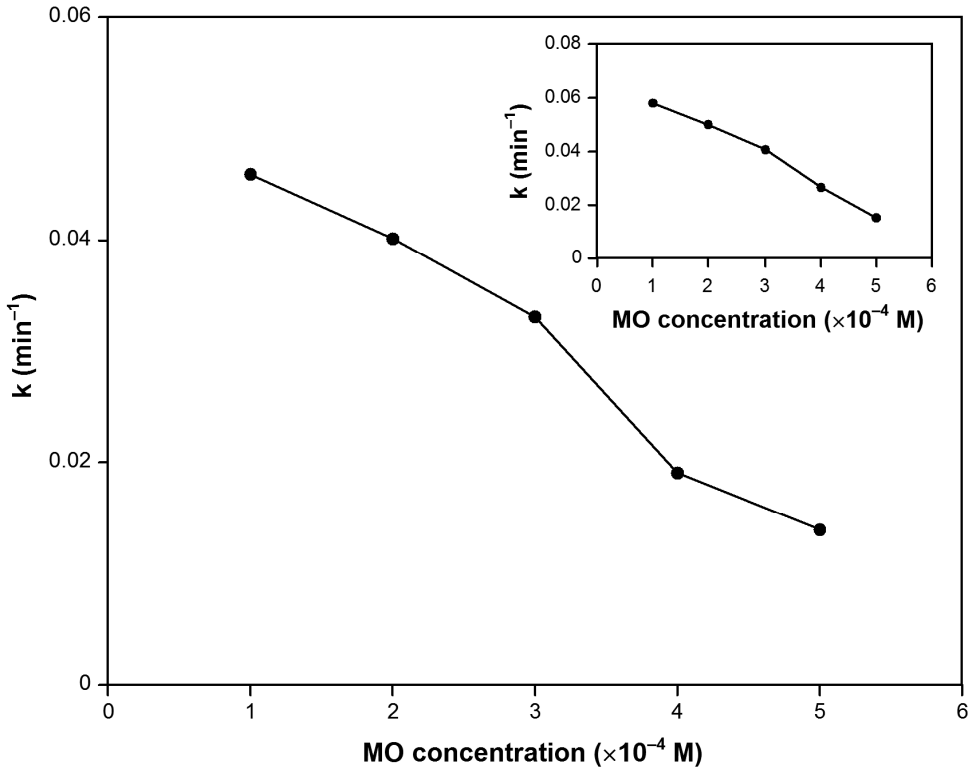

Figure S4 Effect of dye concentration (degradation). 2 wt% Ag-ZnO/$Fe_2V_4O_{13}$ = 3 g L^{-1}, airflow rate = 8.1 mL s^{-1}, pH = 7.0, irradiation time = 15 min, $I_{UV} = 1.381 \times 10^{-6}$ einstein L^{-1} s^{-1}. Inset shows effect of dye concentration (decolorization).

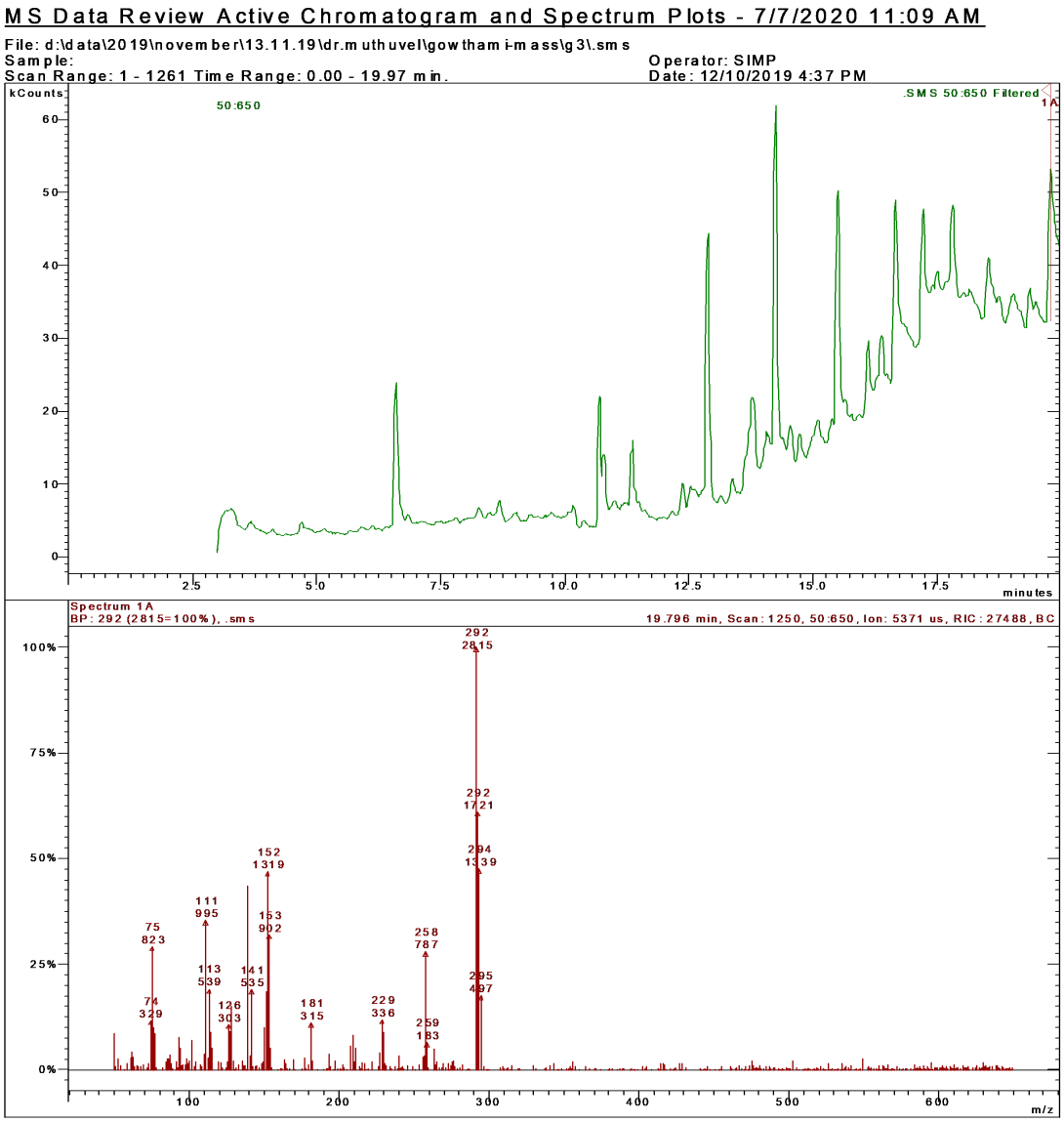

Figure S5. GC-MS spectrum of intermediate $C_{13}H_{13}N_3O_3S$ (D1)R.T-19.796

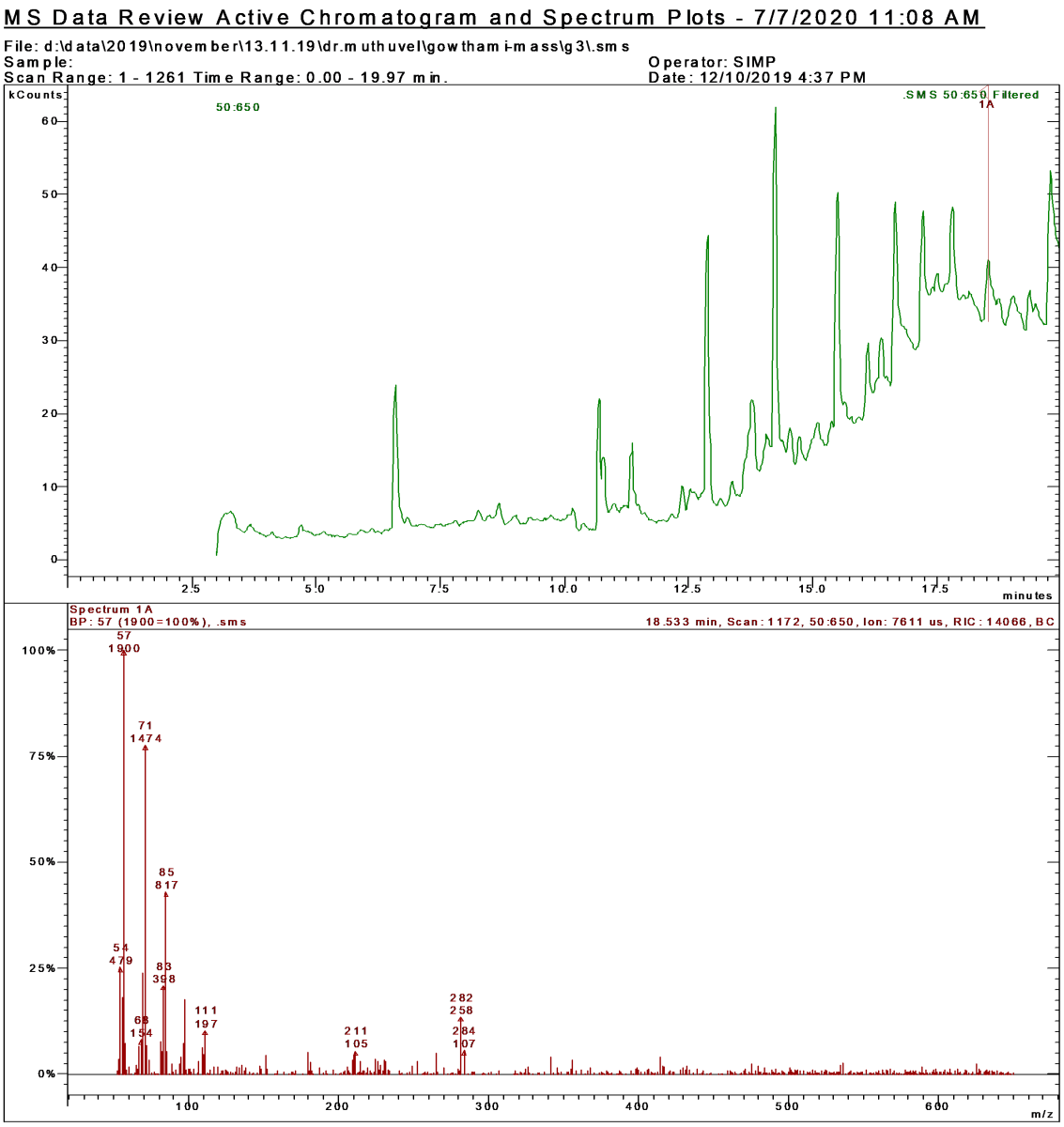

Figure S6. GC-MS spectrum of intermediate $C_{12}H_9N_2NaO_3S$ (D2)R.T-18.533

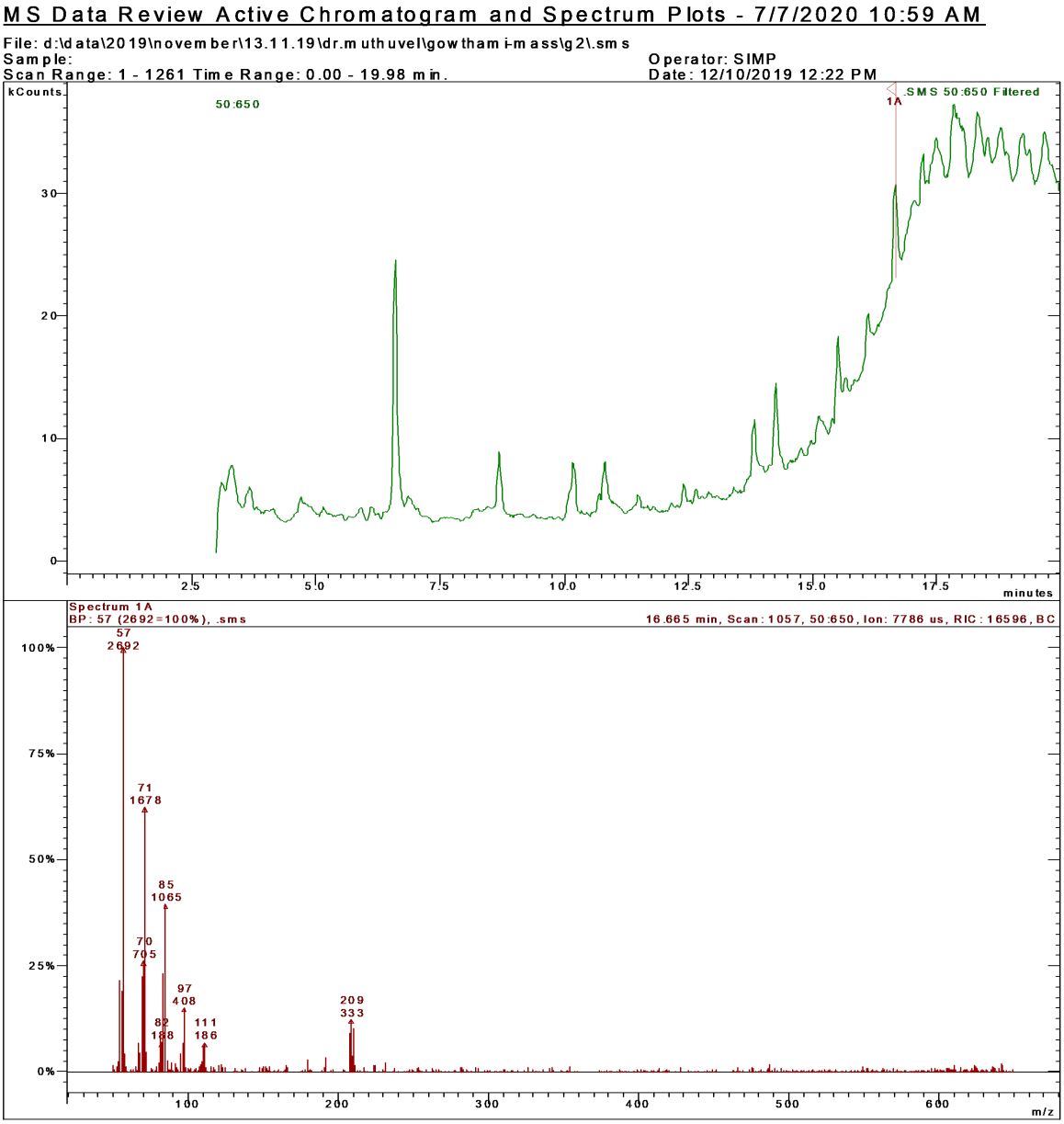

Figure S7. GC-MS spectrum of intermediate $C_6H_5N_2NaO_3S$ (**D3**), R.T-16.665

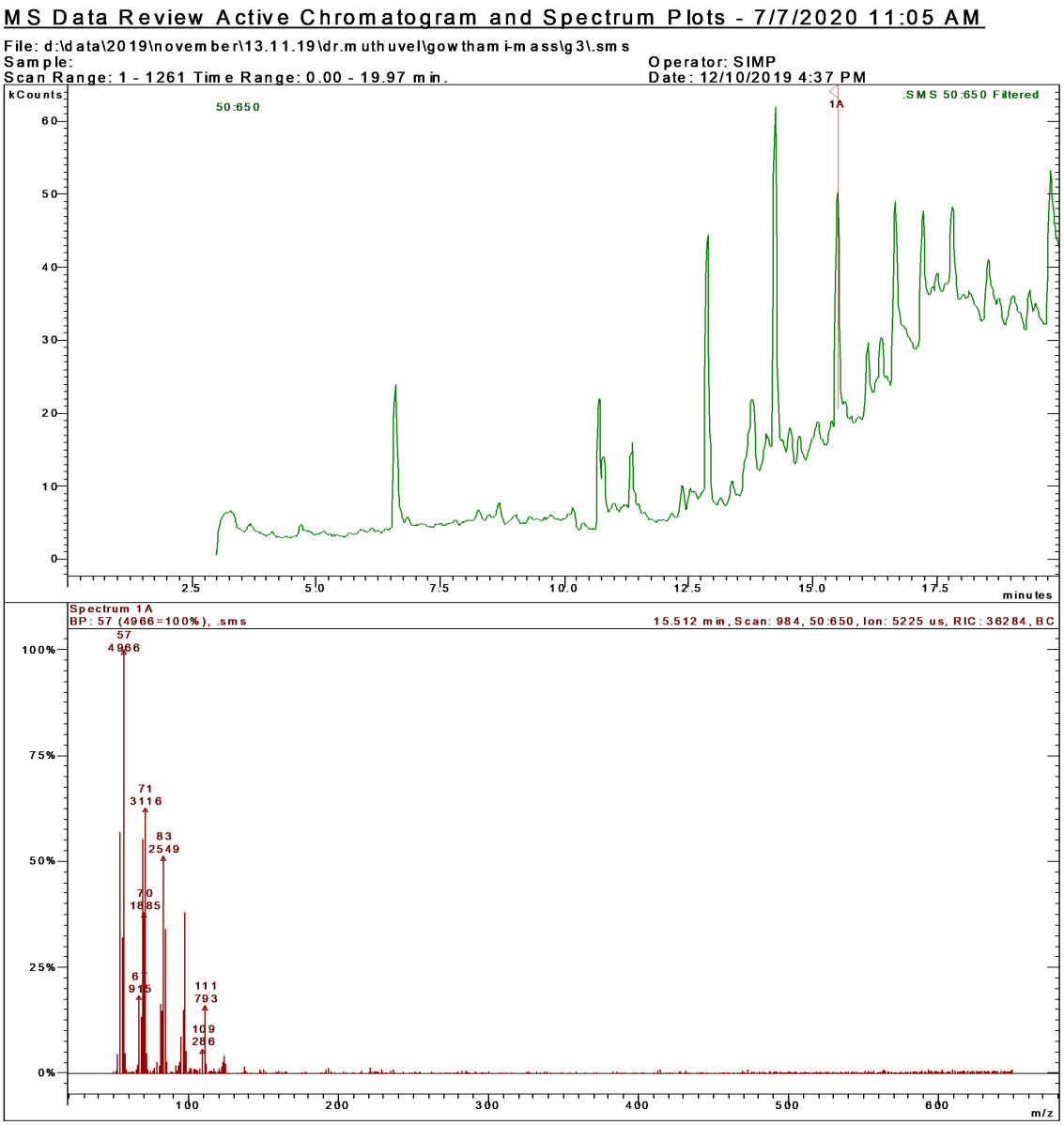

Figure S8. GC-MS spectrum of intermediate C_6H_7NO (**D4**), R.T-15.512

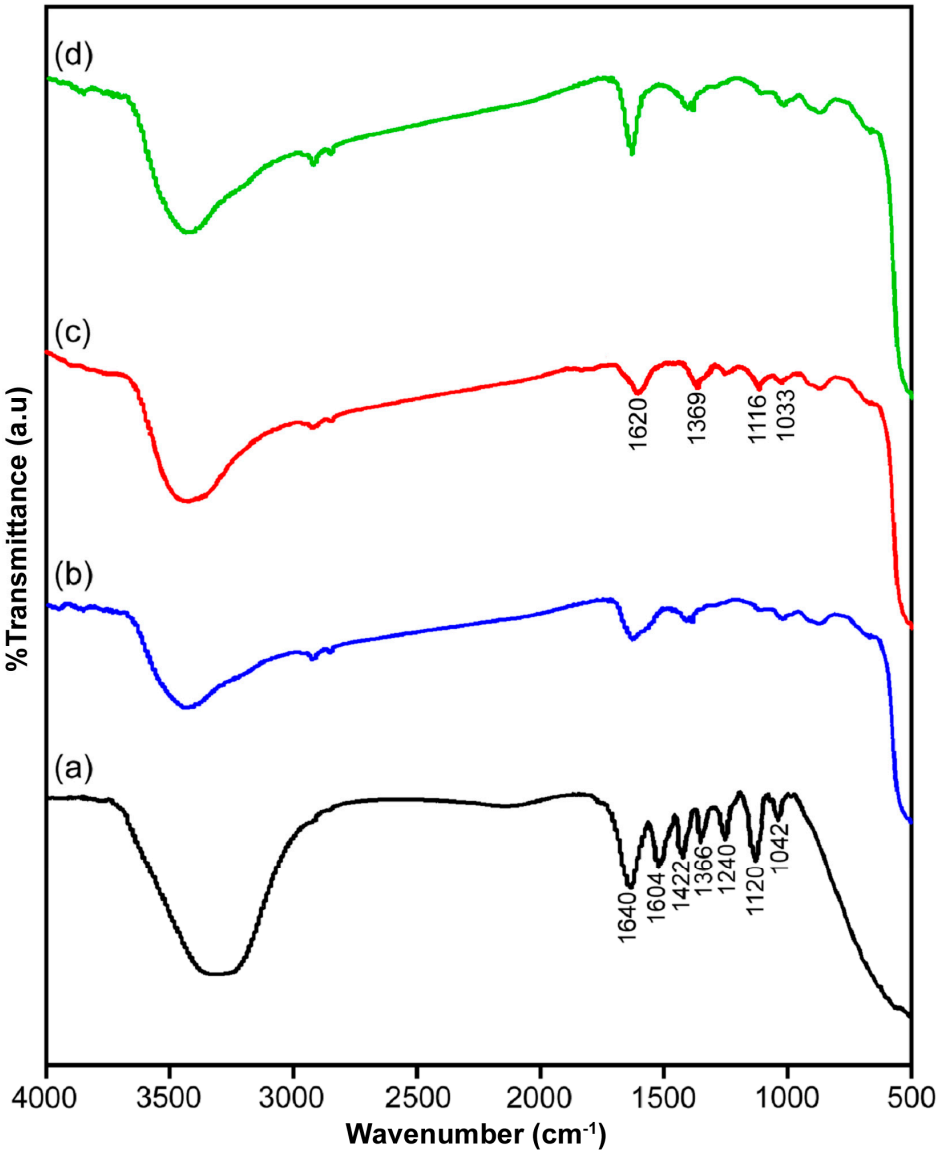

Figure S9. FT-IR spectra of a) MO, b) 2 wt% Ag-ZnO/$Fe_2V_4O_{13}$, c) 2 wt% Ag-ZnO/$Fe_2V_4O_{13}$ after MO dye adsorption, and d) 2 wt% Ag-ZnO/$Fe_2V_4O_{13}$ after complete degradation of MO dye under UV-A light irradiation.