Summary

Phase pure α-, β- and γ-Bi$_2$O$_3$ are prepared by the chemical precipitation method using bismuth nitrate as precursor. The phase purity is confirmed by the X-ray diffraction analysis. The surface morphology and the BET surface area of the samples are determined using HR-SEM analysis and Micromeritics ASAP 2020 apparatus. The bulk resistance and capacitance of the samples are determined from the Nyquist plot by measuring the a.c. excitation response with varying frequency. The indirect band gaps of the samples are determined from the reflectance spectra using the Kubelka-Munk function. The degradation activities of all the samples are carried out using the azo dye, methyl orange as the model pollutant. The kinetics of degradation are analyzed using the pseudo first and second order equations.

The role of surfactant oleic acid in the preparation of phase pure α-Bi$_2$O$_3$ is studied. By comparing the results of phase pure α-Bi$_2$O$_3$ prepared without and with surfactant it is identified that the band gap, surface area and degradation activity are modified with the preparation methodology. The degradation activity is higher for the sample prepared without surfactant (71.1 %) than that of the sample prepared with surfactant. This is due to the reduced band gap of 2.734(1) eV for phase pure α-Bi$_2$O$_3$ compared to that of the sample prepared by the surfactant oleic acid at room temperature (3.303(3) eV). Even though the band gap of α-Bi$_2$O$_3$ prepared with surfactant at an annealing temperature of 600 ºC (2.374(3) eV) is lower than that prepared at room temperature its degradation efficiency is lesser because of the lower surface area. This proves that the surface area also plays an important role in the photocatalytic degradation of methyl orange. The pseudo first order rate constant is higher (0.0046(2) min$^{-1}$) for the sample having higher degradation effect.
The inclusion of tartaric acid as surfactant in the preparation of phase pure $\beta$-$\text{Bi}_2\text{O}_3$ increases the BET surface area with a reduction in the band gap which paves way for the higher photocatalytic degradation efficiency (95.1 % in 180 min) than that prepared without surfactant (59.7 % in 240 min). $\beta$-$\text{Bi}_2\text{O}_3$ prepared using tartaric acid as surfactant shows higher degradation efficiency than that of $\alpha$-$\text{Bi}_2\text{O}_3$ prepared with and without surfactant. This proves that the band gap, surface area and degradation efficiency varies with the phase.

By and large, while comparing $\alpha$, $\beta$ and $\gamma$-$\text{Bi}_2\text{O}_3$ the photocatalytic degradation of $\gamma$-$\text{Bi}_2\text{O}_3$ is higher and faster. Even though the $\alpha$ and $\gamma$-$\text{Bi}_2\text{O}_3$ prepared without surfactant have the equal value of band gap, the BET surface area of $\gamma$-$\text{Bi}_2\text{O}_3$ (1.1594 m$^2$/g) is higher with smaller crystallite size ($\approx 47$ nm) compared to that of $\alpha$-$\text{Bi}_2\text{O}_3$ having a surface area of 0.6998 m$^2$/g and a crystallite size of $\approx 104$ nm. $\beta$-$\text{Bi}_2\text{O}_3$ prepared with tartaric acid as surfactant have higher surface area (13.5636 m$^2$/g) compared to $\alpha$- and $\gamma$-$\text{Bi}_2\text{O}_3$ but its degradation efficiency is less than $\gamma$-$\text{Bi}_2\text{O}_3$. It is attributed to the crystal structure of $\gamma$-$\text{Bi}_2\text{O}_3$ which has higher symmetry compared to $\beta$-$\text{Bi}_2\text{O}_3$. From this it is noted that the degradation property varies with the crystal structure, band gap and crystallite size.

After photocatalytic degradation most of the samples get converted into $\text{Bi}_2\text{O}_2\text{CO}_3$ which proves that the mineralization products during degradation are CO$_2$ and water. They can be brought to their original phase pure form by annealing the sample at the same temperature of preparation.
Future work

Phase pure $\gamma$-$\text{Bi}_2\text{O}_3$ will be prepared using surfactant so as to improve the photocatalytic efficiency further. Suitable dopants will be selected in a manner for the purpose of stabilization of $\text{Bi}_2\text{O}_3$ after photocatalytic degradation. Noble metals will be added to improve the efficiency of photocatalytic degradation in lesser time. Degradation will be carried out for some other dyes, industrial waste etc. to move the work from laboratory scale to industrial level.