Abstract

In this study, highly toxic and persistent in nature organochlorine and organophosphorus pesticides (Endosulfan and Dimethoate respectively) were used as the agrochemical pollutant, and CeO_2-ZnO, CdS, $Cu_{2-x}S$ and $Ni_xZn_{1-x}S$ doped with CeO_2-ZnO nanocomposites were individually used to degrade these pesticides. Organophosphorus and organochlorine pesticides are the most commonly used pesticides in agriculture. These pesticides are most persistent in nature and remain in soil and food for a long time. CeO_2-ZnO nanocomposite has the advantage of having a low band gap as compared to only cerium oxide and the doping of metal sulfide further lower the band gap, thus resulting in better optical and photocatalytic properties of nanocomposites. The redox coupling of Ce^{4+}/Ce^{3+} and formation of oxygen vacancies in cerium oxide play a key role in its photocatalytic activity. In this study, metal sulfide doped CeO_2-ZnO nanocomposite show high photocatalytic activity for the degradation of pesticides.

CeO_2-ZnO nanocomposites are synthesized with the magnetic stirring method and hydrothermal method. The varying pH of CeO_2-ZnO nanocomposites during synthesis reaction helped to evaluate the appropriate reaction parameters for synthesis. It was observed that the crystallite size of nanocomposites slightly changes with an increase in pH of the reaction, but the hydrodynamic particle size of nanocomposites was smallest for the nanocomposite prepared at pH 9. FTIR results showed fewer impurities in samples prepared at higher pH. CeO_2-ZnO nanocomposites prepared with the hydrothermal method at pH 9 have nano-polyhedral CeO_2 structures deposited on spear shape ZnO structures. These CeO_2-ZnO nanocomposites were further used for the synthesis of metal sulfide (CdS, $Cu_{2-x}S$, $Ni_xZn_{1-x}S$) doped CeO_2-ZnO nanocomposites. The doping of CdS, $Cu_{2-x}S$, $Ni_xZn_{1-x}S$ on CeO_2-ZnO nanocomposites was done by using surfactant assisted hydrothermal method. All the metal sulfide doped nanocomposites were prepared by using the same reaction conditions, i.e., time, temperature, dopant concentration and zwitterionic surfactant (SB3-12).

Abstract

The properties of all these nanocomposites (CdS, Cu_{2-x} S and $Ni_xZn_{1-x}S$ doped with CeO_2-ZnO nanocomposite) were evaluated by using different characterization techniques including FTIR, XRD, PL, SEM, TEM, DRS-UV/Vis, and a nanoparticle size analyser. It was found that the concentration of dopant has affected the crystal structure of CeO_2-ZnO nanocomposite. The powder XRD results were elaborately studied with the help of Rietveld refinement using software EXPGUI and GSAS to determine the crystal structure and phase analysis of prepared nanocomposites. The further crystal structure studies were done by using VESTA 3 and Diamond 4 software.

The powder XRD results show the change in peak position and intensity after the doping of metal sulfides. In CdS doped CeO_2-ZnO nanocomposites, the XRD peaks shifted to higher 2θ angle due to changes in lattice structure. A characteristic peak of $Cu_{1.97}S$ was observed at $2\theta = 37°$, in XRD pattern of $Cu_{2-x}S$ doped CeO_2-ZnO nanocomposites and a gradual change in intensity at $2\theta = 36.2°$ (101) was observed with change in dopant concentration. Similar change in intensity with variation of dopant concentration was observed in powder XRD patterns of $Ni_xZn_{1-x}S$ doped CeO_2-ZnO nanocomposites at $2\theta = 31.8°$ (100). The peak intensity was unusually high and increased as the concentration of dopant precursor was decreased. The incomplete phase detection of dopants was the result of weakly crystallized and highly dispersive nanoparticles deposited on the surface of the base material.

The photocatalytic activity results showed that all metal sulfide doped CeO_2-ZnO nanocomposites efficiently degraded Endosulfan as compared to Dimethoate. CdS doped CeO_2-ZnO nanocomposites showed highest rate 164.9×10^{-3} min^{-1} for the photodegradation of Endosulfan. Whereas, $Ni_xZn_{1-x}S$ doped CeO_2-ZnO nanocomposites showed highest rate 25.5×10^{-3} min^{-1} for the photocatalytic degradation of Dimethoate pesticide. The number of oxygen vacancies increased in metal sulfide doped nanocomposites which may have been resulted from lattice expansion of CeO_2-ZnO nanocomposites, the particle size decreases and catalytic activity increased. The presence of oxygen vacancies was observed in photoluminescence spectra of nanocomposites. The number of oxygen vacancies were calculated from lattice constant of nanocomposites.

Abstract

The further work will be done on the metal sulfide doped CeO_2-ZnO nanocomposites with different atomic ratios ($Ce_xZn_{1-x}O_{2y}$) and with different reaction conditions. The hydrothermal synthesis method can be replaced with microwave assisted method to save time. These nanocomposites are unique in their chemical composition and structure. More advanced techniques than conventional powder XRD such as neutron diffraction can be used to evaluate the structural properties of nanocomposites and submit in ICDD database. These nanocomposites can be used for degradation of other pesticide