Combined effects of adsorption and photocatalysis by hybrid TiO$_2$/ZnO-calcium alginate beads for the removal of copper

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**Abstract**

The use of nanosized titanium dioxide (TiO$_2$) and zinc oxide (ZnO) in the suspension form during treatment makes the recovering and recycling of photocatalysts difficult. Hence, supported photocatalysts are preferred for practical water treatment applications. This study was conducted to investigate the efficiency of calcium alginate (CaAlg) beads that were immobilized with hybrid photocatalysts, TiO$_2$/ZnO to form TiO$_2$/ZnO–CaAlg. These immobilized beads, with three different mass ratios of TiO$_2$:ZnO (1:1, 1:2, and 2:1) were used to remove Cu(II) in aqueous solutions in the presence of ultraviolet light. These beads were subjected to three cycles of photocatalytic treatment with different initial Cu(II) concentrations (10–80 ppm). EDX spectra have confirmed the inclusion of Ti and Zn on the surface of the CaAlg beads. Meanwhile, the surface morphology of the beads as determined using SEM, has indicated differences of before and after the photocatalytic treatment of Cu(II). Among all three, the equivalent mass ratio TiO$_2$/ZnO–CaAlg beads have shown the best performance in removing Cu(II) during all three recycling experiments. Those TiO$_2$/ZnO–CaAlg beads have also shown consistent removal of Cu, ranging from 7.14–62.0 ppm (first cycle) for initial concentrations of 10–80 ppm. In comparison, bare CaAlg was only able to remove 6.9–48 ppm of similar initial Cu concentrations. Thus, the potential use of TiO$_2$/ZnO–CaAlg beads as environmentally friendly composite material can be further extended for heavy metal removal from contaminated water.

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**Keywords:** Alginate, Heavy metals, Photocatalyst, Immobilization, Titanium dioxide, Zinc oxide

**Introduction**

Heavy metal-laden wastewater has gained considerable attention due to its potential threat to both humans and the environment. Various efforts have been devoted towards removing heavy metals from wastewater. The non-degradable nature and persistency of heavy metal often render physical and chemical approaches ineffective, thus leading to the attenuation of heavy metals in various compartments of the environment. Prevailing wastewater treatment techniques, which include chemical precipitation, coagulation, chlorination, membrane filtration, adsorption, ion-exchange, and electrochemical treatment technologies has somehow been ineffective to completely remove heavy metals from wastewater, which causes secondary issues (Chong et al., 2010). For example, chlorination produces hazardous by-products, while chemical precipitation generates large amount of sludge and its disposal causes long-term environmental nuisance (Aziz et al., 2008). Hence, a simplistic alternative is necessary to either remove or convert heavy metal cations into non-toxic forms, mainly to combat their ceaseless accumulation in the environment.

Photocatalysis employs semiconductors (or photocatalysts), such as titanium dioxide (TiO$_2$) and zinc oxide (ZnO) for the