ELECTROSYNTHESIS OF ZINC OXIDE-COPPER OXIDE SUPPORTED ON MESOSTRUCTURED SILICA NANOPARTICLES FOR PHOTOCATALYTIC DECOLORIZATION OF METHYL ORANGE

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Specially dedicated to Aboh and Ma,

Che Jusoh bin Talib and Zahrah binti Mat,

To my beloved siblings, nephew and niece

'Thank you for the endless support during my ups and downs'

&

To my beloved one,

'Thank you for always be there and wait for me patiently

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ABSTRACT

Photodecolorization of dyes using heterogeneous catalyst is an important process in wastewater treatment. In this study, an electrochemical method was used to load zinc oxide and copper oxide onto mesostructured silica nanoparticles (CuO-ZnO/MSN). The catalysts were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX), transmission electron microscopy (TEM), nitrogen (N_2) adsorption-desorption, Fourier transform infrared (FTIR), ^{29}Si magic angle spin nuclear magnetic resonance (^{29}Si MAS NMR), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis/DRS), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), photoluminescence (PL) and cyclic voltammetry (CV). The effects of Zinc (Zn) loading, alkaline treatment of MSN and Copper (Cu) loading were investigated for photocatalytic decolorization of methyl orange (MO) dye. Then, the optimization study was performed by response surface methodology (RSM) and the potential of the best synthesized catalyst was tested on decolorization of simulated dye wastewater. From the result, 5 wt% ZnO loaded on MSN (ZnO/MSN) showed the highest photodecolorization rate (9.93×10^{-2} h^{-1}) compared to 1 and 10 wt% ZnO/MSN, due to good dispersion of ZnO on the MSN surface. The alkaline treatment of MSN to load 5 wt% of ZnO catalyst (ZM) of using ammonium hydroxide (NH_4OH) (0.5-2.0 M) demonstrated that ZM prepared under 1.0 M NH_4OH was the best catalyst that improved the photodecolorization rate up to 3.87×10^{-1} h^{-1}. The formation of silicon-oxygen-zinc (Si-O-Zn) with new silicon-oxygen-silicon (Si-O-Si) bonds and creation of oxygen vacancies became the main factors that enhanced the photocatalytic performance. The introduction of Cu as a second metal (1, 3 and 5 wt%) onto ZM catalyst (C-ZM) showed the existence of a synergistic effect between both metal oxides by increasing the formation of Si-O-metal bonds, oxygen vacancies and lowering band gap energy. The high decolorization rate of MO was achieved (1.282 h^{-1}), which resulted in 99.5 % of photodecolorization when using 1.0 g L^{-1} of 3 wt% CuO (3C-ZM) at pH 2 of MO solution. From the RSM experiments, a complete decolorization of MO was predicted (99.99 %) at the optimum conditions of pH 3.5 using 1.6 g L^{-1} of 4 wt% CuO (4C-ZM) catalyst. Lastly, the high decolorization of simulated dye wastewater (>75 %) using CuO-ZnO/MSN catalyst proved that the modifications of ZnO would have great significance in the synthesis and developing the various catalysts for wastewater treatment as well as for other applications.

ABSTRAK

Fotopenyahwarnaan bahan pewarna menggunakan pemangkin heterogen telah menjadi salah satu proses yang penting dalam rawatan air sisa. Dalam kajian ini, satu kaedah elektrokimia telah digunakan untuk menyediakan pemangkin zink oksida dan tembaga oksida yang dimuatkan pada mesostruktur silika nanozarah (CuO-ZnO/MSN). Pemangkin telah dicirikan menggunakan pembelauan sinar-X (XRD), emisi medan mikroskopi elektron penskanan-tebaran tenaga sinar-X (FESEM-EDX), mikroskopi pancaran elektron (TEM), penjerapan-penyahjerapan nitrogen (N_2), spektroskopi inframerah transformasi Fourier (FTIR), ^{29}Si putaran sudut ajaib resonans magnet nukleus (^{29}Si MAS NMR), spektroskopi cahaya-nampak ultrungu-penyerapan reflektif spektroskopi (UV-vis/DRS), spektroskopi fotoelektron sinar-X (XPS), resonans putaran electron (ESR), sinar pendarcahaya (PL) dan kitaran voltammetrik (CV). Kesan muatan zink (Zn), rawatan alkali pada MSN dan muatan tembaga (Cu) telah dikaji terhadap fotopenyahwarnaan metil jingga (MO). Kemudian, kajian pengoptimuman dilakukan menggunakan kaedah respon permukaan (RSM) dan potensi pemangkin terbaik yang disintesis telah diuji ke atas penyahwarnaan air sisa pewarna simulasi. Daripada hasil kajian, 5 wt% ZnO/MSN menunjukkan kadar fotopenyahwarnaan tertinggi (9.93×10^{-2} h^{-1}) berbanding dengan 1 dan 10 wt% ZnO/MSN, ini adalah disebabkan oleh serakan yang baik daripada 5 wt% ZnO pada permukaan MSN. Rawatan alkali pada MSN untuk memuatkan 5wt% ZnO (ZM) menggunakan ammonium hidroksida (NH_4OH) (0.5-2.0 M) menunjukkan bahawa ZM yang disediakan menggunakan 1.0 M NH_4OH adalah pemangkin terbaik yang telah menambahbaik kadar fotopenyahwarnaan sehingga 3.87×10^{-1} h^{-1}. Pembentukan silikon-oksigen-zink (Si-O-Zn) dengan ikatan silikon-oksigen-silikon (Si-O-Si) baru, dan juga pembentukan kekosongan oksigen menjadi faktor utama yang meningkatan prestasi fotopemangkinan. Kemasukan Cu sebagai logam kedua (1, 3 dan 5 wt%) pada pemangkin ZM (C-ZM) menunjukkan bahawa kesan sinergi antara kedua-dua logam oksida dengan peningkatan pembentukan ikatan Si-O-logam, kekosongan oksigen dan merendahkan tenaga jurang jalur. Kadar penyahwarnaan yang tinggi telah dicapai (1.282 h^{-1}), dengan penyahwarnaan 99.5 % apabila meggunakan 1.0 g L^{-1} pemangkin 3 wt% CuO (3C-ZM) pada pH 2 larutan MO. Daripada kajian RSM, penyahwarnaan lengkap MO telah diramal (99.99 %) pada keadaan optima pH 3.5 menggunakan 1.6 g L^{-1} pemangkin 4 wt% CuO (4C-ZM). Akhir sekali, penyahwarnaan air sisa pewarna simulasi yang tinggi (>75 %) menggunakan pemangkin CuO-ZnO/MSN membuktikan bahawa modifikasi ZnO membawa makna yang besar dalam penyediaan dan pembangunan pelbagai pemangkin untuk rawatan air sisa dan juga aplikasi lain.