Preparation of PAN-Fe fibrous catalysts and their application to photo-assisted degradation of the azo dyes in the presence of hydrogen peroxide

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Photo-assisted Fenton reactions is widely used in the degradation of the dyeing wastewater in the past two decades, but have been limited because they are only used at the acidic pH range and the Fe ions remained in aqueous solutions were discharged directly into the environment. In order to overcome these limitations, in this work, polyacrylonitrile (PAN) fiber was modified with hydroxylamine hydrochloride in aqueous NaOH solution, and then impregnated in FeCl$_3$ solution for obtaining the Fe-modified PAN fiber (PAN-Fe fiber). The total Fe content (C$_{Fe-PAN}$) on the surface of PAN-Fe fiber was determined using a Na$_2$EDTA-based titrimetric method. Composition and morphology of PAN-Fe fiber were characterized using FT-IR, XPS and SEM, respectively. Moreover, PAN-Fe fiber was used as the heterogeneous catalyst for the decoloration of some typical soluble anionic azo dyes such as C.I. Reactive Red 195 in the presence of H$_2$O$_2$ under irradiation by a specifically designed photocatalytic reactor. A few factors affecting the preparation of PAN-Fe fiber such as CP% (the degree of conversion from cyano group to amidoxime group of PAN fiber) and FeCl$_3$ concentration were investigated. In addition, the photocatalytic degradation and mineralization of the dyes in the PAN-Fe fiber and H$_2$O$_2$ were examined by UV-Vis spectrum and TOC measurements.

The results indicated that there is a good linear relationship between CP% and C$_{Fe-PAN}$. And increasing CP% and FeCl$_3$ concentration in aqueous solution caused a significant increment in C$_{Fe-PAN}$ when preparing PAN-Fe fiber and the optimum FeCl$_3$ concentration was observed to be 0.05 mol/L, led to the formation of PAN-Fe fiber containing maximum amount of iron. Consequently, it is believed that C$_{Fe-PAN}$ of PAN-Fe fiber is highly dependent on the number of amidoxime group of PAN fiber and FeCl$_3$ concentration. On the other hand, the decoloration percentage and TOC removal of C.I. Reactive Red 195 increased significantly with increasing C$_{Fe-PAN}$ on the surface of PAN-Fe fiber, implying that the photocatalytic decomposition of the azo dye could be remarkably accelerated in the presence of the high C$_{Fe-PAN}$-containing fibrous catalyst. More importantly, the decoloration percentage and TOC removal of C.I. Reactive Red 195 was not dramatically reduced at alkaline pH rang of 8 to 10, suggesting that the azo dye could be effectively decomposed in at alkaline medium. This indicated that dyeing effluent might be treated with PAN-Fe fiber as photocatalyst without pH adjustment in the future application.

Keywords: Polyacrylonitrile fiber; Ferric ion; Photocatalysis; Azo dye; Degradation