

Treatment of the Mixture of Heavy Metal and Organic Wastewaters by Cementation and Fenton-like Processes

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ABSTRACT

The purpose of this study is to explore the treatment of individual or/and mixture of Cu²⁺ and dye (Orange G) wastewaters by cementation and Fenton-like processes within a column test with Fe powder as a sacrificial metal. The removal behaviors of pollutants are investigate at various operating conditions (solution pH values, doses of Fe powder and H₂O₂, flow rates, and initial concentrations of pollutants) to evaluate the treatment efficiencies. Experimental results showed that the decoloration rate of Orange G in aqueous solutions by cementation and Fenton-like processes increased with increasing doses of Fe powder and H₂O₂, with decreasing solution pH values and flow rate. The optimum doses of Fe powder and H₂O₂, are 0.5 gram and 34mg/L, respectively, while the removal of dye reached above 99%. Metal oxides was found to be deposited on FeO powder surface to decrease the pore space, then to reduce the flow rate, and increased the retention time. Based on the analytical results of SEM, it was found that the deposit types and pore sizes of FeO powder which were determined to be the main factors to treatment efficiency of pollutants were different to various reaction solution systems. The acidic erosion of FeO powder by H⁺ was found to be retarded by the deposition of dye, organic intermediates, and Cu²⁺ onto FeO powder surface, then decreased the release rate of Fe²⁺ in the reaction solutions. In the Cu²⁺/FeO column test, the utilization of FeO within the fluidized-bed system was found to be larger than that in the fix-bed system. The breakthrough curve of Cu²⁺ by cementation and Fenton-like processes can be well described by the BDST adsorption model indicating that the rate-determine-step of this system could be FeO surface reactions.

Keywords : Fenton-like ; cementation ; BDST model

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REFERENCES

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