Comparative Study of 2,4-Dichlorophenoxyacetic Acid Adsorption onto Alkali-Activated Carbon Nanotubes and Activated Carbon

Hue Hoang Kim (huehus@gmail.com) (Chemical Command, Hanoi, Vietnam)
Anh Lam Vinh (anhlamcnxl@gmail.com) (Chemical Command, Hanoi, Vietnam)
Cam Le Minh (camlm@hnue.edu.vn) (HNUE, Hanoi, Vietnam)

Background/Objectives. Herbicides are among the most severe pollutants and Vietnam war's remaining consequences at Bien Hoa, Phu Cat and Da Nang airports. The total volume of contaminated soil and sediment is about 700,000 m^3. The main ingredients of the contaminating herbicides are 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and dioxin. To date, Vietnam and the US have completed the remediation of 90,000 m^3 of contaminated soil and sediment by in-pile thermal desorption technology at Da Nang airport. 227,500 m^3 of contaminated soil and sediment have been temporarily isolated in a landfill at the Phu Cat, Bien Hoa and Da Nang airports. The remaining volume of contaminated soil and sediment requires a feasible technology for the remediation. However, all present technologies in Vietnam such as in-pile thermal desorption, isolating land-filling, soil washing, create solution of 2,4-D, 2,4,5-T and dioxin as byproducts, which need a further treatment by adsorbent materials.

Activated carbon (AC) is a traditional adsorbent with large specific area, and a microporous and mesoporous structure. Carbon nanotubes are advanced materials with mesoporous structure and carbon atoms' unpaired π electrons, which could participate in π-π electron interaction with π electrons in 2,4-D, 2,4,5-T and dioxin. Therefore, the comparative study on the adsorption of 2,4-D onto alkali-activated carbon (CNT-K) and activated carbon (AC) has been implemented.

Approach/Activities. CNT-K was prepared by chemical activation of pure carbon nanotubes (CNT) with potassium hydroxide (KOH) in a tube furnace at 800˚C in nitrogen stream. CNT and KOH were in a 1:5 ratio (w/w). AC's trademark name is the Shirasagi-Z1, a powdered product of Japan Enviro Chemicals, Ltd. The characteristics of materials were investigated by nitrogen adsorption-desorption at 77K. Adsorption isotherm and kinetics studies of 2,4-D on the carbon adsorbents were conducted for a range of aqueous concentrations from 25.615 to 151.756 mg L^{-1} of 2,4-D. These studies were conducted at 10, 20, 30 and 40˚C with 1 g L^{-1} of absorbent. The concentration of 2,4-D in solution was determined by a high-performance liquid chromatography (Agilent, US) with a UV-vis detector operated at 280 nm. The mobile phase consisted of acetonitrile, water and acetic acid (50:49:1, v/v/v) at a flow rate of 1mL min^{-1}.

Results/Lessons Learned. The Freundlich model was concluded to be the best model for the adsorption equilibrium, based on average relative error, compared to Langmuir and Temkin models. The Freundlich constant (K_F), which represents the adsorption capacity, was always greater for CNT-K than for AC across the range of temperatures examined in this study. For example, the K_F of CNT-K and AC were 48.90 and 46.43, respectively, at 30°C. The adsorption capability of CNT-K was higher than that of AC, even though the specific area of CNT-K (539 m^2 g^{-1}) was lower than the specific area of AC (1 560 m^2 g^{-1}). This could be due to the π-π interaction between CNT-K and 2,4-D. CNT-K was efficient at reducing 2,4-D from the concentration of 25.615 mg L^{-1} to lower than 0.1 mg L^{-1} at 10°C and 20°C within 2 hours. The kinetic assays indicated the adsorption of 2,4-D onto CNT-K and AC followed the pseudo-second order and Weber-Morris equation with three stages: film diffusion, intraparticle diffusion and mass action, but mainly governed by intraparticle diffusion. The adsorption of 2,4-D onto CNT-K and AC was a spontaneous and exothermic process with characteristics of physical adsorption, based on the observed thermodynamic conditions. Increased temperatures are predicted, therefore, to hinder adsorption and the

rate of 2,4-D removal from solution by CNT-K and AC. CNT-K is a promising material for the remediation of 2,4-D, 2,4,5-T, and dioxin contaminants in solution.