KINETIC AND THERMODYNAMIC STUDY OF CHLOROBENZENE ADSORPTION FROM AQUEOUS SOLUTIONS ONTO GRANULAR ACTIVATED CARBON

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Abstract — The adsorption of chlorobenzene (CB) from aqueous solutions using granular activated carbon (GAC) of different particle sizes was studied at temperatures from 283 to 303 K. Experimental kinetic values were fitted to a hyperbolic expression, which corresponds to the pseudo-second-order kinetic model. The model predictions are satisfactory in the whole range of particle sizes. Adsorption was found to be governed by intraparticle diffusion. For the adsorption system studied, mass transfer resistance becomes low enough at particle sizes below 1.68 mm to allow an adequate intraparticle transport of solute to the adsorption sites on sorbent surface. Isotherm data were fitted to Langmuir, Freundlich and Redlich-Peterson models. The equilibrium uptake capacity increased with temperature, indicating the endothermic nature of the process. The apparent isosteric heat of adsorption was determined by means of the Clausius–Clapeyron equation being in the 88-288 kJ/mol range.

Keywords — Chlorobenzene, adsorption, activated carbon, kinetics.

I. INTRODUCTION

Chlorobenzene (CB) belongs to a group of ordinary contaminants of water. It can be found in the effluents of many industries such as dyestuff, pesticides and rubber industries in which CB is commonly used solvent. It causes an unpleasant taste and odor, even at low concentration (Environment Protection Agency, 1985) and as other chlorinated benzenes has carcinogenic effects in humans (Chowdhury and Viraraghavan, 2009), so that in Spain guidelines on maximum allowable concentrations in drinking water are in the order of parts per billion (Real Decreto, 2003).

Adsorbents such as activated carbon (AC) are widely used for the removal of aromatic compounds from aqueous effluents in drinking water production, as well as in the tertiary treatment of wastewater plants (Zhu et al., 2011). Several cheaper adsorbents such as fly ash, silica gel and clay materials have also been applied for organic compound removal (Ahmed and Ram, 1992). Although some studies illustrate the important need of clay materials treated by chemical or physical processes as adsorbents for the removal of organic pollutants and pesticides from water (van den Heuvel and van Noort, 2004; Yapor et al., 2005), in general terms, it has been reported that the uptake capacity of activated carbon is effective for hydrophobic pollutants and poorly water soluble compounds as chlorobenzene (Croue et al., 1999). The high adsorption capacities of activated carbons are usually related to their high surface area, pore volume, and porosity (Tsai et al., 2001).

Granular activated carbon (GAC) is being used as an alternative to powdered activated carbon because its use in beds permits high adsorptive capacity and the process control, allowing the filling of the column or the regeneration of exhausted activated carbon. Moreover, GAC has excellent adsorption capacity for many undesirable substances, specially odorous compounds or organic compounds frequently present before finished water as chlorinated benzenes. The adsorption of chlorinated benzenes in liquid phase has been scarcely studied in the literature, due to the difficulty of its analysis and its volatility (Wang and Lee, 1998). It is well known that the adsorption of these hydrocarbons takes place in monolayer when activated carbon is used, whereas it occurs as multilayer when resins are used (Gusler et al., 1993). In a recent article, the adsorption of chlorobenzene with powdered activated carbon was studied at 25 ºC considering the influence of two experimental parameters, initial CB concentration and AC dose (Lin et al., 2012). Data for aqueous CB adsorption in GAC analyzing the influence of particle size were not found in the open literature.

The objective of this work was to study the adsorption kinetics, equilibrium and thermodynamics of chlorobenzene in aqueous solutions onto activated carbon of various particle sizes. The influence of adsorption temperature is a relevant issue, since adsorption temperatures may significantly vary depending on the source of wastewater, so the study was made at various temperatures and the isosteric heat of adsorption was also determined.

II. METHODS

A. Materials

Activated carbon manufactured from lignite by DARCO® (Sigma-Aldrich) was used in this study. Particle size varied in the range of 0.250 to 1.68 mm. Activated carbon was previously washed with distilled water, dried in oven at 105 ºC for 24 hours and then stored in a desiccator. Textural properties were determined by N₂ adsorption-desorption at 77 K. The measured values of Brunauer-Emmett-Teller (BET) surface area and pore volume were 600 m²/g and 0.95 cm³/g, respectively. Due to the low water solubility of chlorobenzene (analytical grade, purity > 99%, UCB), stock solutions were prepared in acetonitrile. Working solutions were prepared by dilution of the stock solution. The quantification of chlorobenzene was carried out by gas chromatography with a flame ionization detector (FID).