CHAPTER I

INTRODUCTION

Chloronitrobenzenes (CNBs) are isomeric substances, which include *m*-, *o*-, and *p*-CNB. They are important intermediates for the production of azo, and sulfur dyes. Moreover, they are used in the synthesis of preservatives, fungicides, pharmaceuticals, pesticides, rubber chemicals and photochemicals (Priegnitz, 1980). They are prepared commercially by either nitration of chlorobenzene (CB) or chlorination of nitrobenzene (NB) depending on the proportions of *m*-, *o*-, and *p*-CNB in desired products. Furthermore, both *o*- and *p*-CNB are being used more than *m*-CNB because of its industrial applications. There are many commercial processes that have been developed for CNB separation, *e.g.* fractionation, crystallization, and adsorption (Demuth *et al.*, 2002).

Crystallization is considered to be commercially attractive since it offers potentially low-energy separation compared with distillation because latent heats of fusion are generally much lower than latent heats of vaporization (Mullin, 2001). However, its drawback is that it does not provide a possible means for complete separation because of the presence of the eutectic point. To obtain higher purity of CNBs, a combination of separation processes has been developed such as the combination of crystallization and fractionation for CNB separation.

The other attractive technique for the separation is adsorption. Adsorption from the liquid phase is used to recover reaction products that are not easily separated by distillation or crystallization. It consists of two main pathways: adsorption and desorption, where FAU zeolites are frequently used as an adsorbent in the chemical industry due to their high selectivity and adsorption capacity. It can decrease energy consumption and provide a high-purity product (McCabe *et al.*, 2005).

In 2010, Yairit studied the influence of feed compositions on precipitate composition and crystallization temperature of CNBs. At the eutectic composition, the precipitates composed of 62.95 wt% *m*-CNB and 37.05 wt% at *p*-CNB. Below the eutectic composition, the precipitates were enriched with 91.08 wt% *p*-CNB, while above the eutectic composition, the precipitates were rich in *m*-CNB, 89.85 wt%. The effects of number of a zeolite showed that the feed solution with 5 grains of the zeolites resulted in the precipitates with high *p*-CNB compositions than that from the solution with 10 grains of the zeolites. The precipitates near the zeolites had *p*-CNB purity higher than those far from the zeolites. For the precipitates in the feed above the eutectic composition, the zeolites can shift the precipitate composition from being rich in *m*-CNB to *p*-CNB. Furthermore, the presence of seeds can induce the crystallization of the precipitates following the phase diagram at the feed composition and the purity of the precipitates decreased with the increase in the number of the seeds. Seeds and zeolites also had a great influence on the crystallization temperature. Nucleation could be induced by using zeolites at a lower temperature than that required for the crystallization without any zeolite.

In this work, effects of adsorbents on the crystallization of the CNBs at the eutectic composition were then focused. Furthermore, attempts to answer why the precipitate compositions were shifted from *m*- to *p*-CNB above the eutectic composition in the presence of the zeolites were made.