CHAPTER I
INTRODUCTION

Chloronitrobenzenes or CNBs are isomeric substances, which are important intermediates in a manufacture of azo and sulfur dyes because they can be converted into commercial dyes by a relatively simple reaction. Moreover, they are used in the synthesis of fungicides, pesticides, pharmaceuticals, photochemicals, preservatives, and rubber chemicals. CNBs can be produced via chlorination of nitrobenzene and nitration of chlorobenzene depending on the proportions of *m*-, *o*-, and *p*-CNB in desired products (Demuth *et al.*, 2002). To obtain specific purity of each isomer required by industry, a choice of separation processes is very critical. Because the boiling points of these isomers are so close, they cannot be separated by distillation (Dunn, 1968). Adsorption and crystallization become attractive.

Liquid phase adsorption consists of two main pathways: adsorption and desorption, in which zeolites are frequently used as an adsorbent. Although liquid phase adsorption is an effective and economic separation process, its mechanisms are highly complex due to the interaction of solid adsorbents, liquid adsorbates, and liquid adsorbents during the separation process. Also, the adsorbent and desorbent selection is very crucial (Kulprathipanja *et al.*, 2002).

Crystallization is one of the cheapest and easiest ways to obtain a pure form of isomers by using the difference in crystallization temperatures; however, it is not a possible means for complete separation of isomeric substances because of the presence of a eutectic point. The maximum purity of precipitate composition is at the eutectic temperature, while the mixture is solid below this point (Rousseau, 1987). To obtain higher purity of CNBs, a combination of separation processes has been developed such as the combination of crystallization and fractionation for CNB separaion.

In 2008, Yensukjit studied static adsorption behavior of *m*- and *p*-CNB mixtures on FAU zeolites (X and Y zeolites) with alkaline earth exchanged cations. The results showed that the adsorption capacities of CNBs on the zeolites partly depended on the acid-base interaction and *m*-CNB was selectively adsorbed by the zeolites more than *p*-CNB due to its higher dipole moment or higher basicity.

Moreover, the adsorption capacities of *m*-CNB and *p*-CNB on the zeolites increased with the acid strength of the zeolites. CaY was the most appropriate adsorbent for the CNB separation because they offered the high adsorption capacity of CNBs and a high *m*-/*p*-CNB selectivity. The work also studied the adsorption applications on the crystallization by using the FAU zeolites, which are NaX, CaX, NaY, and CaY. The results revealed that at 65 wt% of *m*-CNB in the feed, the addition of the zeolites could shift the precipitate composition to be rich in *p*-CNB with the higher purity and NaY gave the highest purity of *p*-CNB in the precipitates. Moreover, there is no effect of adsorption and composition gradient during the experiment, and the purity of *p*-CNB in the precipitates depended on their position and type of zeolites (Yensukjit, 2008).

In this research, the effect of FAU zeolites on the crystallization of *m*- and *p*-CNB was further studied. First, the effect of feed compositions without a zeolite on the precipitate composition was studied. Furthermore, the effect of adding a zeolite on the precipitate composition and crystallization temperature was investigated. The results of crystallization with and without zeolite were then compared.