CHAPTER I
INTRODUCTION

I.1 Background

The presence of ammonia in aquatic environment causes a serious problem for aquatic biota especially for fish. In water, the ammonia presence in the ionized form (NH_4^+) and un-ionized form (NH_3), and both of these substances are present in equilibrium condition according to the following equation [1]:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$

The total concentration of the ionized ammonia (NH_4^+) and un-ionized ammonia (NH_3) in water is defined as total ammonia nitrogen (TAN), and at a certain concentration, the un-ionized ammonia (NH_3) is lethal for fish. The equilibrium concentration of ammonia in the water is affected by the pH and temperature. At high pH, the equilibrium condition (equation 1) will shift towards the formation of ammonia, while at low pH the formation of ammonium ion (NH_4^+) is dominant. For aquatic biota such as fish, the ammonium ion is relatively non-toxic compared to the ammonia. Ammonia also predominates when temperature is high while the ammonium ion predominates at low temperature.

In the aquaculture industry the quality of water is the most important parameter for the continuation of the industry. One of the important parameters for the quality of water is TAN. It is the major nitrogenous waste product of fish and also results from the decomposition of organic matter. As natural byproduct of fish metabolism, ammonia can accumulate easily in aquatic system and it has the tendency to block the transfer of oxygen from gills to the blood nerve system and cause gill damage. The excess ammonia in water also destroys the fish mucous producing

membrane and damages the internal intestinal surfaces. The presence of excessive amounts of ammonia in the aquatic environment causes eutrophication.

A number of processes are currently available for the removal of TAN from the aquatic environment, and the most widely used process is the adsorption process. This process offers several advantages than other available processes, such as high removal efficiency, the adsorbent can be re-used, can be applied for a wide range of concentration, and cost effective process. One of the available natural adsorbents which is widely employed for the removal of ammonia from aquatic environment is zeolite. Zeolite ismicroporous and aluminosilicate mineral which possesses the structure like three dimensional honey comb with negative charge within the pores. It contains hydrated alumino-silica with symmetrically stacked alumina and silica tetrahedral. The presence of alkali cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) in the frame work of zeolite stabilize the structure, and in the aquatic condition, these cations are also exchangeable with other cations from the solution [2, 3].

The disadvantage of using natural zeolite as adsorbent for the removal of NH_4^+ ion from aqueous solution is low adsorption capacity, and most of them have the adsorption capacity less than 10 mg/g [4-10]. The low adsorption capacity and removal efficiency are still the main problem for industrial application of natural zeolites in aquaculture, water and wastewater processes. In order to improve its adsorption capacity, a modification using chemical treatment processes is necessary. The modification of natural zeolites can be conducted using various kinds of chemicals such as acid, alkali, and salt [11-14]. Microwave irradiation [15] and heat treatment [16] methods were also employed to increase the

adsorption capacity of natural zeolites. Leyva-Ramos *et al*. [11] modified natural zeolite with sodium chloride to remove ammonium from aqueous solution and the result clearly indicates that natural zeolite enriched with Na^+ more preferentially exchanged by NH_4^+ than other the other alkali cations. The modification using acid solution is seldom used because acid treatment causes de-alumination process, in which it removes Al^{3+} ions from the zeolite structure and decreasing the ion exchange process [3].

In this study a modification of natural zeolite with sodium hydroxide combined with thermal treatment is proposed. To the best of our knowledge, report about zeolite modified with this method is rarely available. The modified zeolite was employed for removal of NH_4^+ ion from aqueous solution and aquaculture system (Koi pond). The adsorption isotherms of ammonium ion onto natural and modified zeolite were obtained at three different temperatures (303.15, 308.15, and 313.15 K). The temperature dependent forms of Langmuir, Freundlich, Sips, and Toth equations were used to correlate the adsorption experimental data. The adsorption kinetics of ammonium ions onto natural and modified zeolite was also studied. Well know pseudo first and second order kinetic models were employed to represent the kinetic data. The removal of ammonium ion from Koi pond system was conducted at dynamic mode. The breakthrough adsorption performances were correlated by Thomas equation.

I.2 Objective

a. To study the effect of zeolite and sodium hydroxide ratio to the ammonium removal from fish pond water.
b. To study the effect of temperature on the adsorption capacity in adsorption process.

c. To obtain the design adsorption system for ammonium ion adsorbed onto zeolite and modified zeolite (kinetic study).
d. To study the Thomas equation for describe the breakthrough curve in the laboratory compare with pond
e. To investigate the influence of sodium hydroxide and zeolite ratio on its characteristics (morphology, surface area, crystal structure and pore volume).

I.3 Problem Limitation

a. The kind of fish is Koi fish in the fish pond of Widya Mandala Catholic University Surabaya, Kalijudan.
b. The kind of zeolite is Ponorogo zeolite.