Adsorption of Tetramethylammonium Hydroxide (TMAH) on Y-type Zeolite

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ABSTRACT

In this study, we applied commercially available Y-type zeolites (NaY) to remove TMAH from aqueous solutions. The results showed that amount of TMAH adsorbed on NaY increased with pH from 2 to 4 but showed insignificant change above 4. The Freundlich isotherm model was better corrected (R^2=0.997) with equilibrium adsorption capacity (q_e) than the Langmuir model (R^2=0.973). The kinetic study indicated that the adsorption behavior is fast and can be described by a pseudo-second-order model (R^2=0.999) with the calculated q_e and rate constant (k) are 28.6 mg/g and 0.0191 g/mg/min, respectively. The spent Y-type zeolites can be easily regenerated by 0.1 M NaCl solution in 20 minutes, and after ten times cyclic experiments, the recovery rate of q_e is 98.8%, which means that this material can be used for long term adsorption-desorption operation. These results reveal that adsorption by NaY zeolite is a potential technique for TMAH treatment.

Keywords: Tetramethylammonium Hydroxide (TMAH); adsorption; desorption; NaY; zeolite

1 INTRODUCTION

Tetramethylammonium Hydroxide (TMAH) is widely used chemicals in many industrials such as manufacture of semiconductors and thin-film transistor liquid crystal displays [1,2]. TMAH solution is toxic and also possesses a strong organic base which may harm the aquatic organisms and cause the eutrophication of aqueous environment[3]. Therefore, it is necessary to find a proper treatment technology for TMAH wastewater.

Adsorption method is effective and simple; it can offer a high reaction rate and less land area usage comparing with traditional biological processes [4,5]. Adsorption process had been widely used to treat with different kinds of pollutants from aqueous, such like metal ions [4,6], and organics[7-9].

Zeolites are porous aluminosilicate minerals containing with exchangeable alkali or alkaline-earth metal ions in the structure framework, which can adsorb and exchange surrounding positive ions easily. Several researchers proved that zeolites have great potential as sorbents for treating with heavy metals [10-12] and ammonium pollutants [13,5]. However, studies on the adsorption of TMAH solution by zeolites are still linited in the past. Thus, adsorption characteristics of TMAH aqueous solution by commercially available zeolites are carried out in this study.

2 MATERIAL AND METHOD

2.1 Sorbent

Commercially available sodium form Y-Type Zeolites(NaY) with SiO_2/Al_2O_3 mole ratio of 5.1 (CBV100, Zeolyst International, PA, USA) were selected as adsorbents in this study. The unit cell size of zeolites was 24.65 Å and the surface area was 900m^2/g. These data were provided by the manufacturer. The raw NaY were dispersed in 60°C 2M NaCl solution with zeolite-solution ratio (Z/S) of 50 g/L and stirred at 120 rpm for 12h pretreatment. After the pretreatment, zeolites was filtrated and washed with deionized water and then dried at 110 °C for 6h. The purpose of the pretreatment was to bring the zeolite sorbents to near homoionic Na-form[4].

2.2 Sorbate

Electronic-grade 25% w/w TMAH aquatic solution (Alfa Aesar, Lancashire, U.K.; 99.9999% purity) was employed to prepare a stock solution containing 1 g/L of TMAH. The stock solution was further diluted with deionized water to the desired TMAH concentrations.

2.3 Batch Adsorption Experiments

Batch adsorption experiments were conducted using 100 mL glass bottles with 0.1 g of NaY and 50 ml of TMAH solution. The glass bottles were sealed and then were mounted in an orbital shaker (model D500, Deng Yng, New Taipei, Taiwan) , which was placed in a temperature-controlled box (model CH-502, Chin Hsin, Taipei, Taiwan) and operated at 25 °C and 200 rpm for 12 h. The glass bottle wall had been tested several times, and the result showed that almost no TMAH uptake was found, which indicated that there was no influence on adsorption experiments. The initial pH of solution was adjusted from 2-11 by 0.1M HNO_3 or 0.1M NaOH in the pH effect study.

The TMAH concentration was determined by an ion chromatography system (model 883 Basic IC Plus, Metrohm, Herisau, Switzerland) with C 4-150/4.0 column. The elute was 10 mM HNO_3 in 7.5% methanol solution at flow rate 1.4 mL/min.

The TMAH adsorption amount of NaY was calculated as follows:

$$q_t = (C_0 - C_t) \times V / m \qquad (1)$$

where q_t is the TMAH adsorption amount of NaY (mg/g); C_0 is the initial TMAH concentration in the solution (mg/L); C_t is the TMAH concentration after certain period of time (mg/L); V is the initial solution volume (L); and m is the NaY mass (g).

2.4 Batch Regeneration Experiments

Testing for regeneration performance of NaY to reduce the cost for the sorbent replacement is important before practical application of NaY for TMAH wastewater treatment. The regeneration of zeolites for heavy metal adsorption was studied in some literatures. Some researchers reported that NaCl solution was recommended regeneration agent for Zn-adsorbed zeolite because of its lower cost and high desorption effectiveness [6]; thus, NaCl solution was selected as regeneration agent in this study.

The batch adsorption experiment with 100 mg/L initial TMAH concentration was carried out at first. As the adsorption reached equilibrium, the TMAH adsorption capacity was measured and then the solution was filtered using a 0.45 μm Nylon filter to collect NaYs. These NaYs were added into NaCl solution with Z/S of 5 g/L and then shacked at 200 rpm and 25 °C in 20 minutes. 10 cycles adsorption/desorption experiment was carried out in this work.

3 RESULTS AND DISCUSSIONS

3.1 Effect of pH

Figure 1 shows the effect of solution pH on TMAH adsorption with initial concentration of 50 mg/L by NaY. It seems that the TMAH adsorption amounts were increased with pH value and without significant change above pH 4.

Since TMAH is permanently ionized over any pH range, the decrease of TMAH uptake in low pH is mainly contributed from surface charge change of sorbent itself. The measured surface charge of NaY was negative in the pH range 4-11, which caused a more electrostatic attraction of TMAH ions.

However, the surface of Y-type zeolites changed to positive gradually when the pH value below 4, which caused an electrostatic repulsion of TMAH. Furthermore, the competition adsorption between H^+ and TMAH ions, and the structure decomposition of Y-type zeolites were both found in lower pH. These phenomena above reveled that TMAH adsorption on NaY is not favorable at lower pH value of solutions.

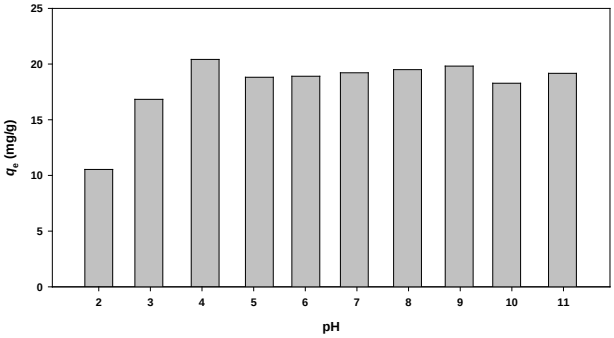

Figure 1 : Effect of solution pH on TMAH adsorption by NaY.

3.2 Adsorption Isotherms

Adsorption isotherms of TMAH by NaY are presented in Figure 2. The experimental data were fitted with Langmuir (Eq(2)) and Freundlich (Eq(3)) equations:

$$q_e = \frac{abC_e}{1 + bC_e} \qquad (2)$$

$$q_e = K_f C_e^{1/n} \qquad (3)$$

Where C_e is the equilibrium TMAH concentration (mg/L); a is the maximum adsorption capacity (mg/g); b is the Langmuir adsorption constant (L/mg); K_f and n are Freundlich constants.

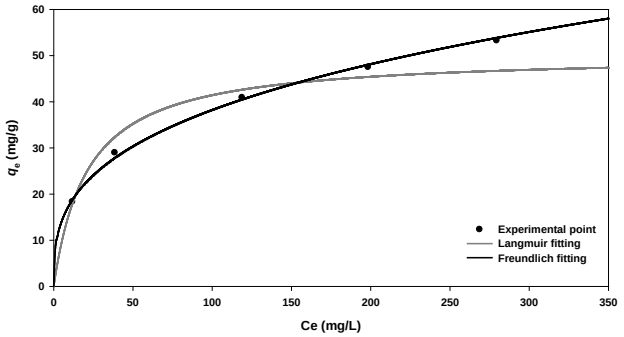

Figure 2 : Isotherms of TMAH adsorption on NaY at 25°C.

The constants of Langmuir and Freundlich isotherm models were obtained from fitting the equations to the q_e and are given in Table 1. It is obvious that Freundlich model fitted much well(R^2=0.997) than the Langmuir model(R^2=0.973), that is, the adsorption of TMAH may

take place at a heterogeneous surface with a non-uniform distribution. The value of n is grather than 1, which indicated that the adsorption behavior is favorable.

Langmuir			Freundlich		
a	b	R^2	K_f	n	R^2
50.26	0.047	0.973	8.25	3.002	0.997

Table 1 : Constants of Langmuir and Freundlich isotherm models

3.3 Effect of Contact Time

Figure 3 shows the effect of contact time on the TMAH adsorption with initial concentration of 100 mg/L by NaY. The TMAH uptake amount (q_t) increased quickly with time and reached equilibrium in 120 min. It can be found that pseudo-second-order kinetic model have better fitting (R^2=0.999). The calculated equilibrium adsorption capacity (q_e) and rate constant (k) of model are 28.6 mg/g and 0.0191 g/mg/min, respectively.

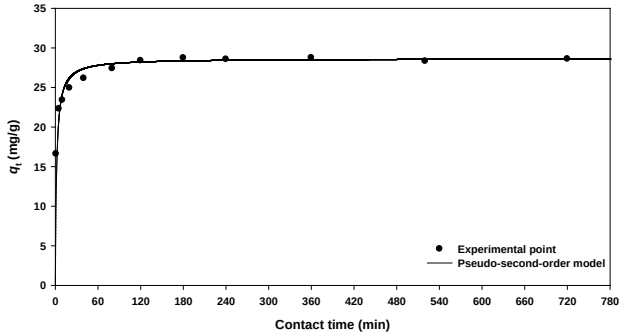

Figure 3 : Effects of contact time on TMAH adsorption via NaY at 25°C.

3.4 Cyclic Adsorption/Desorption Study

In the 10 times cyclic adsorption/desorption experiment, the 0.1M NaCl solution was used to regeneration agent of spent NaY. Figure 4 shows the adsorption capacity after each regeneration process, it seems that the capacities were not decrease significantly and were still preserved in the following regeneration process. After 10 times of regeneration, the recovery rate of q_e is 98.8%, which means that this material can be used for long term adsorption-desorption operation.

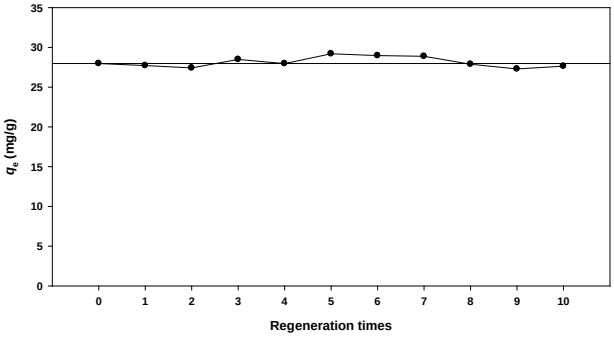

Figure 4 : Cyclic TMAH adsorption on Y-type zeolite via 0.1 M NaCl regeneration

4 CONCLUSION

The commercially available NaY zeolite was selected as sorbents to study adsorption characteristics of TMAH from aqueous solution. The amount of TMAH adsorbed on NaY increased with increasing pH from 2 to 4 but showed insignificant change above 4. The Freundlich isotherm model has better correction with q_e than the Langmuir model. The adsorption kinetics was fast and could be discribed by pseudo-second-order kinetic model. In the regeneration study, spent NaY could be regenerated by 0.1 M NaCl solution in 20 minutes and the q_e was presvered after 10 cycles of adsorption/desorption operation.

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