Journal of Environmental Chemical Engineering 3 (2015) 807–814

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Statistical analysis and optimization of ammonia removal from aqueous solution by zeolite using factorial design and response surface methodology

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ARTICLE INFO

Article history:
Received 21 January 2015
Accepted 26 March 2015
Available online 28 March 2015

Keywords:
Ammonia
Zeolite
Adsorption
Kinetics
Isotherm
Factorial design
Response surface methodology

ABSTRACT

The ability of zeolite as a low-cost adsorbent for ammonia removal from aqueous solution was studied through batch adsorption experiments. The results showed that zeolite was effective in eliminating ammonia from aqueous solution. Factorial design and response surface methodology were applied to evaluate and optimize the effects of pH, adsorbent dose, contact time, temperature and initial ammonia concentration. Low pH condition was preferred with the optimum pH found to be 6. High adsorbent dose generated high removal rate and low adsorption capacity. Results of factorial design and response surface methodology showed that temperature was not a significant parameter. The model prediction was in good agreement with observed data (R^2 = 0.969). The optimum Q_e was 22.90 mg/g achieved at pH 7 and initial TAN concentration of 3000 mg/L. The adsorption kinetics followed the Pseudo-second order kinetic model (R^2 = 0.998). Equilibrium data were fitted to Langmuir and Freundlich isotherm models with Freundlich model (K_f = 2.24 L/mg, $1/n$ = 0.28) providing a slightly better predication (R^2 = 0.992). The $1/n$ value of less than 1 indicated that the removal process was favorable.

Introduction

Ammonia (NH_3) is the most commonly encountered nitrogen compound in liquid phase. Ammonia can exist in liquid phase either in unionized form (NH_3) or ionized form (NH_4^+) depending on the pH and temperature. It is common in aquatic chemistry to refer to and express the sum of the two as simply ammonia or total ammonia nitrogen (TAN) [1]. The presence of high concentration ammonia can contribute to eutrophication in rivers and lakes, and dissolved oxygen depletion in receiving water bodies. Also, unionized ammonia is toxic to most fish species even at low concentrations (0.53–22.8 mg/L) [2]. Extremely high ammonia concentrations (1500–5000 mg/L) can cause failure in wastewater treatment process due to the inhibition effect [3,4].

Conventional methods for ammonia removal from aqueous solution include biological treatment, air stripping, ion-exchange and adsorption [5]. Traditional biological processes incorporate nitrification and denitrification and they do not perform well to the shock ammonia loading [6]. Air stripping provides satisfactory results in high pH conditions where most ammonia is in unionized form (NH_3) [7]. Finding efficient and low-cost material for ammonia removal has become one of the research focuses in the field of ammonia removal from liquid phase. Recently, ion-exchange and adsorption processes have received more interests as possible treatments due to relatively simply operation and high removal efficiency [8]. Previous studies have reported that natural zeolite could be a promising material as a means of ammonia removal from aqueous solution [9–12].

Natural zeolite is a porous material with large surface area, high adsorption and cation exchange capacity and cation selectivity [13]. The major mineral component of natural zeolite is clinoptilolite which has a high affinity for ammonium nitrogen [14]. It has a classical three-dimensional alumina silicate structure [13]. Natural zeolite is abundant and widely available in nature at low-cost. As such, it could be an alternative material for the expensive ion-exchange resins or adsorption materials such as activated carbon and could be a promising material for ammonia removal in water and wastewater treatment [15,16]. Previous studies have confirmed the ability of removing ammonia from aqueous solution by zeolite. It was reported by Du et al. that the adsorption capacity (Q_e) of a Chinese natural zeolite was 14.50 mg/g at a pH 6 and initial ammonia concentration of 92.4 mg/L and a zeolite dose of 5 g/L [12]. Higher Q_e (25.93 mg/g as ammonium nitrogen) was achieved by Sarioglu using natural

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http://dx.doi.org/10.1016/j.jece.2015.03.025
2213-3437/

Turkish zeolite at pH 4 and initial ammonia concentration of 885 mg/L with a zeolite dose of 10 g/L [17].

The main objective of this study was to evaluate and optimize ammonia removal by zeolite using factorial design and response surface methodology (RSM). The effect of different operational factors including pH, zeolite dose and temperature were also investigated. In addition, reaction kinetics and isotherms were modeled using existing common models.

Material and methods

Zeolite characteristics

The natural zeolite used in this study was a commercial product obtained from a fertilizer company. The selected zeolite type used in this study was clinoptilolite type which is the most common and abundant type of natural zeolite with widespread industrial and environmental applications. Both chemical and physical properties were provided by the producer. Rock analytical data (chemical analysis) of the zeolite sample is summarized in Table 1 [18]. 85% of the mineralogical content was clinoptilolite. The main components are SiO_2 and Al_2O_3. Bulk density and cation exchange capacity were reported to be 880–960 kg/m^3 and 1.4–1.65 mEq/g, respectively. The natural zeolite sample was in granular form and particle size ranged within 0.3–2.0 mm. The surface area of the natural zeolite is 24.9 m^2/g.

Zeolite sample was first washed with distilled water (DW) to remove fine dust and all water soluble residues, and then it was oven dried at 105 °C for 12 h. Then, based on the results of preliminary tests, NaCl solution (2 mol/L) was used to wash the zeolite for a second time and zeolite was dried for another 4 h at 25 ± 1 °C. Zeolite was washed with DW one last time and dried [19].

Synthetic ammonia solution

Synthetic ammonia stock solution of 3000 mg/L as TAN was prepared by dissolving 5.72 g analytical grade NH_4Cl into 500 mL distilled water. Then the stock solution was diluted with DW to achieve desired concentration.

Analytical methods

The concentration of TAN in the liquid phase was determined by Salicylate method (Method 10205) TNTplus 832 test using a Hach DR6000 spectrophotometer. Solid phase concentration was calculated using the mass balance according to Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e is the mass of TAN adsorbed per unit mass of zeolite (mg/g), C_0 and C_e are initial and equilibrium concentration of TAN in the liquid phase (mg/L), respectively. V is the volume of solution (L) and m is the mass of zeolite (g).

The ammonia removal efficiency was obtained by Eq. (2):

$$\text{TAN removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where C_0 and C_e are initial and equilibrium concentration of TAN in the liquid phase (mg/L), respectively.

Kinetics experiments

4.0 g of zeolite was added to 400 mL synthetic ammonia solution with TAN concentration of 1000 mg/L in 1 L Erlenmeyer flask. The reactor was immediately subject to the agitation at 130 rpm. TAN concentrations were measured at 1, 2, 5, 10, 20, 30, 60, 120, 240, 360, 720 min after the shaking started. Results from a preliminary set of experiments (presented below), showed the maximum ammonia removal occurred at pH 6. Thus, a pH 6 was selected for the kinetic studies.

Batch adsorption experiments

Preliminary batch adsorption experiments were conducted to determine the effect of pH and optimum zeolite dose. Different amounts of zeolite were added to 40 mL of synthetic ammonia solution with TAN concentration of 1000 mg/L in 50 mL centrifuge tubes. pH of the solution was adjusted by addition of 1N NaOH or 1N HCl. Samples were agitated by the shaker at 130 rpm for 24 h which was confirmed by another preliminary test that was more than enough to reach equilibrium. Then solid phase and liquid phase were separated by centrifuging the sample at 8000 rpm for 10 min. TAN concentrations in the solution were then measured as explained above.

For the main phase of experiments, batch adsorption tests were conducted based on a factorial design at different pH, temperature and initial ammonia concentration. A 3^2 factorial design with pH (pH), temperature (T) and initial TAN concentration in the solution (TAN) as the independent variables was implemented. Each independent variable was coded at two levels between −1 and +1 at the designed ranges based on preliminary studies and some previous studies. The values of the independent variables are presented in Table 2. pH 7 was selected as the lower limit as it is neutral condition and there was no considerable difference in ammonia removal as pH increased from 3 to 7. pH 9.2 was chosen as the upper limit as it is close to the pK_a of ammonia. Room temperature of 26 °C and hot room temperature of 32 °C were coded as −1 and +1 level, respectively. Initial TAN concentration of 300 mg/L was selected as the lower limit while 3000 mg/L was the upper limit. Each set of experiment was carried out in triplicate to ensure the reliability of the outcome response.

For each run, in order to obtain data to study isotherms, 1.0 g of zeolite was added into 40 mL of synthetic ammonia solution in 50 mL centrifuge tubes, containing concentrations in the range of 300–3000 mg/L as TAN. Samples were agitated in the shaker at 130 rpm for 24 h to achieve equilibrium. Then samples were

Table 1
Rock analysis of zeolite.

Constituent	Value (%)
SiO_2	67.40
Al_2O_3	10.60
FeO_3	1.70
MgO	0.45
CaO	2.23
Na_2O	0.59
K_2O	4.19
TiO_2	0.27
P_2O_5	0.10
MnO	<0.01
Loss of ignition (at 925 °C)	11.40

Table 2
Independent variables of the experimental design.

Independent variable	Symbol	Coded level	
		−1	+1
pH	pH	7	9.2
Temperature (°C)	T	26	32
Initial TAN conc. (mg/L)	TAN	300	3000