บทความวิจัย

การวิเคราะห์โครงสร้างของซีโอไลต์ธรรมชาติ และการประยุกต์ใช้ในการบำบัดแอมโมเนียมในน้ำเสีย

Structural Characterization of Natural Zeolite and Its Applications in Removal of Ammonium for Wastewater Treatment

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Abstract

The natural zeolite, as an effective adsorbent derived from Songkhla province, was characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectroscopy. The results reveal that the XRD pattern of the zeolite corresponds to the clinoptilolite compound with the molecular formula of $(Na, K, Ca)_5Al_6Si_{30}O_{72}.18H_2O$. The XRF analysis shows the elemental compositions of the zeolite confirming the structural data obtained by the XRD method. Consecutively, the investigations of adsorption of ammonium contaminated in wastewater on the zeolite have been carried out. Wastewater samples from 2 frozen seafood factories in Songkhla province were collected. To measure ammonium contaminated in wastewater, the phenol-hypochlorite method was applied. The results show that the amounts of ammonium decrease and pH values increase after treatment with zeolite. The optimum adsorption time is 2 hours and the ratio of zeolite per water sample is 2g/100ml. Ammonium was removed from wastewater samples with the best removal efficiency of 78.79%. Consequently, the natural zeolite is successfully applicable for the removal in ammonium of wastewater from frozen seafood factories.

บทคัดย่อ

การวิเคราะห์โครงสร้างของซีโอไลต์ธรรมชาติ จากจังหวัดสงขลา ซึ่งเป็นสารดูดซับที่มีประสิทธิภาพโดยเทคนิคเอ็กซ์เรย์ดิฟแฟรคชั่น (XRD) และเอ็กซ์เรย์ฟลูออเรสเซ็นซ์ (XRF) ผลจากการวิเคราะห์ด้วยวิธีเอ็กซ์เรย์ดิฟแฟรคชั่นพบว่าโครงสร้างของซีโอไลต์ธรรมชาติสอดคล้องกับสารประกอบคลิโนปทิโอไลต์ โดยมีสูตรโมเลกุล คือ $(Na,K,Ca)_5Al_6Si_{30}O_{72}.18H_2O$ และผลจากการวิเคราะห์ด้วยวิธีเอ็กซ์เรย์ฟลูออเรสเซ็นส์ ทำให้ทราบเปอร์เซ็นต์ของธาตุที่เป็นองค์ประกอบของซีโอไลต์นี้ ซึ่งสามารถยืนยันข้อมูลทางโครงสร้างที่ได้จากวิธีเอ็กซ์เรย์ดิฟแฟรคชั่น ได้ทำการศึกษาความสามารถในการดูดซับแอมโมเนียมที่ปนเปื้อนในน้ำเสียของซีโอไลต์ธรรมชาติโดยทำการเก็บตัวอย่างน้ำเสียจากโรงงานอาหารทะเลแช่แข็งในเขตจังหวัดสงขลา 2 โรงงาน ในการวิเคราะห์หาปริมาณแอมโมเนียมที่มีปนเปื้อนในน้ำเสียได้ใช้วิธีฟีนอลไฮโปคลอไรต์ (Strickland and Parsons, 1972) ผลการศึกษาพบว่าปริมาณของแอมโมเนียมลดลง แต่มีค่าความเป็นกรดสูงขึ้น หลังนำน้ำเสียมาผ่านการดูดซับด้วยซีโอไลต์ ระยะเวลาที่เหมาะสมที่สุดในการแช่ซีโอไลต์ในน้ำตัวอย่างคือ 2 ชั่วโมง และปริมาณซีโอไลต์ต่อน้ำตัวอย่างที่เหมาะสมที่สุดคือ 2 กรัมต่อ 100 มิลลิลิตร ประสิทธิภาพการกำจัดปริมาณแอมโมเนียมออกจากน้ำเสียมีค่าดีที่สุดเป็น 78.79% ดังนั้นซีโอไลต์ธรรมชาตินี้สามารถนำไปประยุกต์ใช้ในการบำบัดแอมโมเนียมในน้ำเสียที่ได้จากโรงงานอาหารทะเลแช่แข็ง และเป็นแนวทางนำเอาซีโอไลต์ธรรมชาติไปใช้ในการดูดซับแอมโมเนียมในน้ำทิ้งแหล่งอื่นๆ ได้

Introduction

Zeolite is crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water and by alkali and alkaline earth cations (normally Na^+, K^+, Ca^{2+} and Mg^{2+}). Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites show special importance in water and gas purification, adsorption and catalysis, and agriculture and aquaculture (Ciambelli et al., 1984; Dyer, 1988; Mumpton, 1988). There are several types of them as natural and synthetic zeolites both zeolites have ability to remove several cations from solutions concerning adsorption and ion exchange features (Dryden, 1984; Tsitsishvili et al., 1992; Zamzow and Murphy, 1992). The main features of zeolites are high level of ion exchange capacity, adsorption, porous structure, molecular sieve, dehydration and rehydration, low density and silica compounds.

One of the widely used methods for waste purification is adsorptional (Gutman, 1978; Limtrakul and Onthong, 1997). In the last 10-15 years, the interest in the zeolites as natural adsorbent for waste waters purification is exceptionally great. In this context they are new raw materials and the fields of application for waste waters purification to a certain extent are not understood.

The widespread applications of cation-exchange and adsorption proposes using natural zeolites were first developed by Ames, 1967 and Mercer et al., 1970 who demonstrated the effectiveness of clinoptilolite for extracting ammonium from municipal, agricultural waste stream and aquacultural industry where water is recirculated. The various aspects of removal of ammonium from aqueous solutions by clinoptilolite have been investigated by many researchers (Jorgensen, 1975; Kim et al., 2005; Sarioglu, 2005; Semmens et al., 1981). Adsorption process with a high affinity for binding ammonium is clinoptilolite, a naturally occurring zeolite. The availability of natural zeolite in many countries facilitates low-cost wastewater treatment by ion-exchange and adsorption systems.

Mineral nitrogen forms, widespread pollutants of natural waters, often enter the hydrogen in ammonium forms that maybe relatively easier to extract from water than the nitrate forms. Among various methods available for ammonium removal from aqueous solution (wastewater) by zeolites via exchange with cations or by adsorption in pores of aluminosilicate systems; both materials seem promising as the most attractive and low cost ion exchangers for the removal of ammonium.

In the aqueous solution, ammonium can exist in either the nonionised form (NH_3) and /or ionised form (NH_4^+) depending on the pH and temperature. Of these two forms of ammonium, only the ionised one can be removed by the ion-exchange process. The ammonium ion-exchange capacity and efficiency for adsorption varies to some extents depending on the presence of another cations in the aqueous phase and initial ammonium concentration (Demir et al., 1998; Gaspard et al., 1983; Lin and Wu, 1996; Singh and Prasad, 1997). The ion-exchange capacity is influenced significantly by chemical and physical pretreatment techniques and loading or regeneration of clinoptilolite. The influence of a pretreatment on ion-exchange capacity varied widely depending on the source of clinoptilolite (Klieve and Semmens, 1980; Sirkecioglu and Erdem-Senatalar, 1995).

The aim of this study is to investigate ammonium removal from wastewaters by using natural zeolite and structural characterization of natural zeolite by using X-ray diffraction and X-ray fluorescence spectroscopic techniques.

Materials and Methods

This study used commercial zeolite purchased from shop in Songkhla province. For characterization of natural zeolite, the X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert MPD, using CuKα radiation source (λ=1.54 nm) at 45 kV and 35 mA. Each sample was measured in the range of $5° \leq 2\theta \leq 120°$ with scanning rate 0.04 2θ/sec at room temperature. The X-ray fluorescence (XRF) analysis was performed on a Philips MagiX WDXRF. Wastewater samples were collected from two frozen seafood factories in Songkhla province, and it had already been filtered when it arrived at the laboratory. To measure ammonium ion in wastewater (before and after the zeolite adsorption treatment), the phenol-hypochlorite method (Strickland and Parsons, 1972) was applied and using spectrophotometic technique. Measurements were made.

Results and discussion

In order to characterize the structure of the natural zeolite, XRD analysis was performed. The XRD pattern is shown in Figure 1. The obtained XRD pattern was compared with the patterns given in the ICDB number. The results reveal that the profile corresponds to the 47-1870 ICDB number of the clinoptilolite compound having molecular formula$(Na,K,Ca)_5Al_6Si_{30}O_{72}\cdot 18H_2O$. For XRF results, the elemental compositions of the zeolite were analyzed as reported in Table 1. It was found that the information obtained by XRF analysis could support the structural data derived by the XRD pattern. The natural zeolite was chosen on the basis of its good ammonium-ion selectivity and potentially low cost. Clinoptilolite is reported to have a classical aluminosilicate cage like structure and therefore it exhibits significant macro porosity. In the nature, the cations present on clinoptilolite are calcium, sodium and potassium. The element compositions of the natural zeolite used in this study are given in Table 1.

For adsorption of ammonium contaminated in wastewater on the zeolite, the ammonium removal efficiency was affected by contact time and ratio of zeolite usage per water sample volume, as listed in Tables 2. The minimum contact time is 2 hours, the removal efficiencies of 78.79% and 43.81% for the 1st and 2nd frozen seafood factories, respectively. And the contact time is 12 hours, ammonium was removed from wastewater samples with efficiency of 78.23% (1st frozen seafood factory) and 53.33% (2nd frozen seafood factory). In adsorption process, the ammonium concentrations have effected to pH value (see Table 3). The ratio of zeolite per water sample volume with 20 g/L is the optimum usage for ammonium treatment. After that, ammonium concentrations after treatment are quite constant, as shown in Figure 2.

Conclusion

We report the fundamental study on the ammonium removal efficiency from wastewater by the natural zeolite, which is very inexpensive adsorbent relative to the synthetic zeolite. The removal of ammonium in wastewater from frozen seafood factories in Songkhla province was demonstrated successfully on a laboratory scale. The adsorption characteristic of ammonium depended not only on the physical properties of the adsorbent itself such as the cation exchange capacity but also on the concentration, existence of exchangeable cation, pH, and contact time. On the basis of the present study, the obtained results can suggest that the use of the natural zeolite as an adsorbent is an efficient and cost-effective method for ammonium treatment of wastewater.

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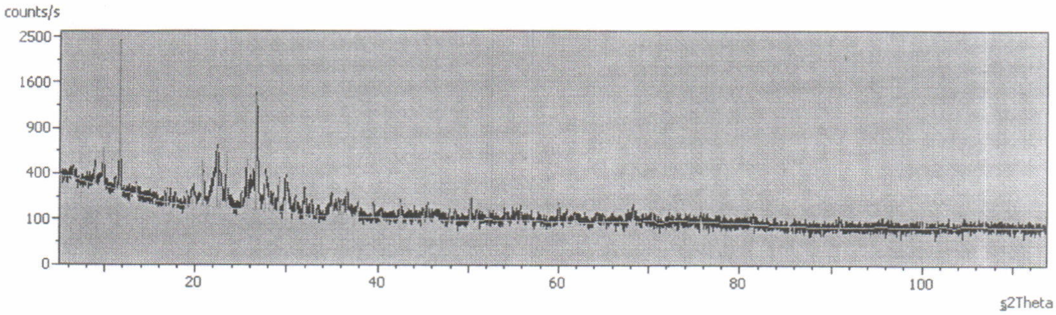

Figure 1. X-ray diffraction pattern of the natural zeolite.

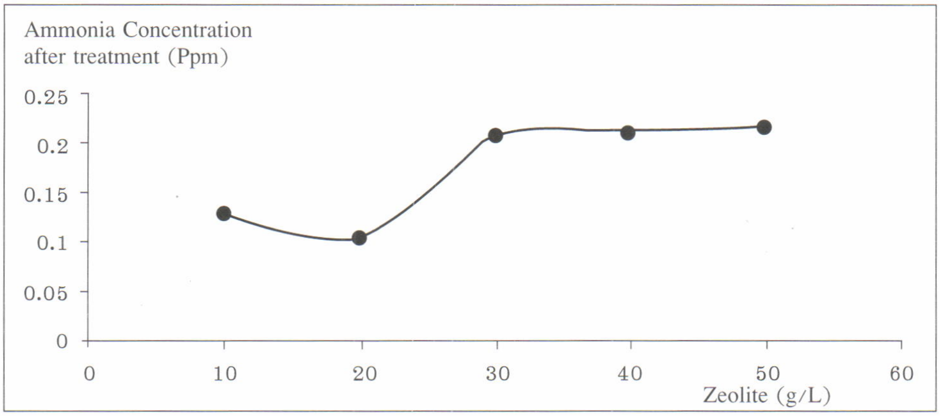

Figure 2. Relationship between ratio of zeolite per water sample volume (g/L) and ammonium concentrations after treatment.

Table 1. The element compositions of the natural zeolite, derived by XRF spectroscopy.

No.	Compound name	Concentration (%)	Absolute error (%)
1	O	44.6834	0.300
2	Na	0.1778	0.002
3	K	0.6838	0.003
4	Al	9.4457	0.020
5	Si	40.4976	0.050
6	S	1.3038	0.006
7	Ca	2.0860	0.020
8	Fe	1.1219	0.006

Table 2. Efficiency of ammonium removal of natural zeolite by varying adsorption time.

Water samples	Adsorption time (hour)					
	2 hour			12 hour		
	Ammonium concentration (ppm)			Ammonium concentration (ppm)		
	Before treatment	After treatment	Removal efficiency (%)	Before treatment	After treatment	Removal efficiency (%)
1st factory	0.5512	0.1169	78.79	0.5512	0.1200	78.23
2nd factory	0.2164	0.1216	43.81	0.2164	0.1010	53.33

Table 3. pH value of sample solution.

Water samples	pH value		
	Before treatment	After treatment	
		2 hour	12 hour
1st factory	4.75	7.09	6.72
2nd factory	5.87	6.70	7.10

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