



## INCREASING THE ADSORPTION OF CLINOPTILOLITE AS TOXIN BINDER BY HEAT TREATMENT

H. ESECELI<sup>1</sup>, M. A. OZCAN<sup>2</sup>, ERGUN DEMIR<sup>3</sup> & T. BILAL<sup>4</sup>

<sup>1</sup>Bandırma Onyedi Eylül University, Faculty of Health Sciences, Bandırma, Turkey;  
<sup>2</sup>Abant İzzet Baysal University, Vocational School of Sureyya Astarci, Bolu, Turkey;  
<sup>3</sup>Balıkesir University, Faculty of Veterinary Science, Balıkesir, Turkey; <sup>4</sup>Istanbul University, Faculty of Veterinary Science, Avcılar, Istanbul, Turkey

### Summary

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Mycotoxins are one of the most important biosafety issues in the chain of animal food production today. Clinoptilolite is an important clay mineral which is dwelled on due to its adsorbent characteristics. In this study, it is aimed to activate the clinoptilolite by increasing the adsorption amount through application of heat treatment at different temperatures and durations. A total of 13 trial samples consisting of one control (non heat-treated) and 12 trial groups, in which 3 different temperatures (300 °C, 450 °C and 600 °C) and 4 different heating durations (15 min, 30 min, 60 min, 120 min) were applied, were analysed in terms of physicochemical properties, and thereby mineral and chemical content as well as physical properties were determined through X-ray diffraction method, XRF spectrophotometer and analyses, respectively. The heavy metal (Pb, Hg, Cd) levels of zeolite and active clinoptilolites were determined in these clinoptilolites activated by total cation exchange capacity (CEC), selectivity and other adsorbent properties such as primary adsorbed gases. As a result, it was observed at the pre-heat treatment trials that adsorption capacity of clinoptilolite, highly activated by applying heat treatment at different temperatures and durations, increased. Therefore, it can be stated that mycotoxin, moisture and gas binding capacity of clinoptilolite can increase about 4 times compared to clinoptilolite produced by means of conventional method.

**Key words:** adsorption, clinoptilolite, heat treatment, toxin binder

### INTRODUCTION

Toxin binders are the substances which are used to minimise the toxicity arising from contaminated mycotoxins transmitted to feeds in the process of reaching to animals from fields. Seven mycotoxins consisting of natural contaminants in feeds and food are further dwelled on. These micotoxins are aflatoxin, zearalenone, ochratoxin A, citrinin, tricothecenes,

patulin, penicillic acid and ergot alkaloids. (Steyn and Stander 1999; Souza *et al.*, 1999; Kaya *et al.*, 2002).

Many substances (activated carbon, polymers such as PVP, aluminum silicate compounds such as diatomaceous earth, HSCAS, etc.) are used to prevent the mycotoxin formation in feeds and its effects on animals. Their effects essentially vary

depending on the adsorption capacity of their molecules, their purity and the characters of the mycotoxins to be bound. Mycotoxin binding capacity of clay minerals vary depending on their properties such as their cation exchange capacity, pH and surface acidity, surface area, number of pores and pore diameter. The structure of clinoptilolite in the form of a cage forms a large internal and external surface area for chemical reactions to ion exchange. The pores inside cover the 50% of its volume. However, in order to utilise these properties, clinoptilolite should be produced and processed by using suitable methods under suitable conditions. Clinoptilolites are natural substances which can hold water, gas and metal ions in an exchangeable situation within themselves, do not contain harmful elements, and can resist to temperature up to 750 C and to acids-bases (pH 1.5–11) (Balevi *et al.*, 1999; Melenova *et al.*, 2003; Demirel *et al.*, 2010). Zeolite ore is micronised in different diameters, and the micronised ore includes chemically-physically bound water and volatile hydrocarbons, and its adsorption capacity remains very low. However, it is possible to activate the zeolite by washing amorphous substances that inhibit transition in the canals and pores of zeolites rich in clinoptilolite, with acid and to increase its porosity and adsorption capacity. In the studies carried out in physicochemistry field, it has been demonstrated that heat-treatment application by airless heating in zeolite treated with acid in such way will contribute to increase porosity and to enhance the toxic substance holding capacity by further activating the zeolite, and thus it will be much higher compared to zeolites that are only micronized and treated with acid. It is stated that adsorption amount of zeolites can also be increased due to the pores

left by water that evaporates when heated at 350–400 °C. (Lee *et al.*, 2000; Hwang *et al.*, 2002; Rozic *et al.*, 2002; Ackley *et al.*, 2003; Cheng *et al.*, 2005; Campos & Büchler, 2007).

## MATERIAL AND METHODS

The study aimed to determine the effects of heating at different temperatures and durations on the basic properties related to adsorption capacity of zeolite. For this purpose, the zeolite treated with HCl acid was obtained from a manufacturer in Bigadic. With the zeolite brought to the R&D laboratory set up as part of the TUBITAK project, a total of 13 samples consisting of one control (non heat-treated) and 12 trial groups in which different temperatures (300° C, 450° C and 600° C) and four different heating durations (15 min, 30 min, 60 min, 120 min) were applied, were generated. Analyses of these prepared samples were performed in laboratories which belong to General Directorate of Mineral Research and Exploration.

Chemical content of non heat-treated natural zeolite was measured by XRF Spectrophotometer, mineral content levels and dioxin levels were determined by total cation exchange capacities of Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, CaO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, A.Za (1050 °C) and pH, heavy metals and CEC value. In heat-treated samples, all other analyzes were performed except mineral content. Physical properties, dispersion in water using Micromeritics ASAP 2020-multipoint, oil absorption, original bleaching, activated bleaching, water absorption, mudding and softening, Pozzolanic activity, true density, apparent porosity, water absorption % values were determined.

## RESULTS

Physical analysis results of non heat-treated zeolite used in the study and clinoptilolites consisting of 12 trial groups in which 3 different temperatures (300 °C, 450 °C and 600 °C) and 4 different heating durations (15 min, 30 min, 60 min, 120 min) were applied, are provided in Table 1 while chemical analysis results are provided in Table 2. According to physical analysis results of non heat-treated zeolite and clinoptilolites treated at different temperatures and durations, dispersion in the water was determined only in the samples CLP 09 – 600 °C/ 15 min. and CLP 12 – 600 °C/120 min while other samples showed no dispersion in the water. Oil absorption level (mL/100 g) was 38.00 in non heat-treated natural CLP 13 while it was determined at the levels of 32.00, 31.90, 36.00, 44.00, 42.00, 45.00, 45.00, 40.00, 42.00, 46.00 and 40.00, respectively in other samples. It has been found that as the temperature and time increase, the oil absorption levels increase. Original bleaching level was at the level of 2.18 in non heat-treated natural CLP 13 while it was determined as 1.73, 1.72, 1.70, 1.60, 1.59, 2.15, 2.16, 1.65, 1.65, 1.63, 1.69, 1.55 respectively in heat-treated samples. It was observed that this level decreased when compared to non heat-treated natural CLP 13 level, and that results close to natural were available only in CLP 06 – 450 °C/30 min and CLP 07 – 450 °C/60 min samples. Original bleaching level was at the level of 1.55 in non heat-treated natural CLP 13 while it was determined as 1.50, 1.45, 1.50, 1.60, 1.58, 1.70, 1.67, 1.48, 1.53, 1.61, 1.55, 1.70, respectively in heat-treated samples. It has been found that the applied heat treatment does not make a significant difference in the activated bleaching levels. Absorption capac-

ity was at the level of 1.55 in non heat-treated natural CLP 13 while it was determined as 25.00, 20.72, 22.00, 27.00, 30.00, 20.00, 21.00, 22.89, 18.63, 24.75, 24.45, 17.67, respectively in heat-treated samples. It has been found that absorption capacity increases along with the heat treatment, but it does not change and decreases in CLP 09 – 600 °C/15 min and CLP 12 – 600 °C/120 min samples. In the analysed samples, it has been determined that heat treatment does not have any effect on mudding and softening.

Pozzolanic activity level was at the level of 5.65 for non heat-treated natural CLP 13 while it was determined as 6.70, 8.36, 6.30, 3.30, 1.20, 9.70, 6.80, 7.70, 7.80, 7.33, 4.74, 3.18, respectively in heat-treated samples. Pozzolanic activity was determined to achieve the highest level especially in CLP 06 – 450 °C/ 30 mins. sample. Apparent density level showed no significant change in heat-treatment applications. Apparent porosity percentage was at the level of 19.10 in non heat-treated natural CLP 13 while this value was determined as 20.00, 38.50, 34.00, 26.00, 26.00, 38.00, 40.00, 33.00, 39.10, 30.12, 29.62, 26.14, respectively in heat-treated samples. The highest apparent porosity percentage was found in CLP 07 – 450 °C/60 min sample. Water absorption percentage was at the level of 17.75 in non heat-treated natural CLP 13 while it was determined as 19.00, 20.40, 22.00, 15.00, 16.00, 17.00, 19.00, 19.00, 16.00, 15.7316 and 22.00, respectively in heat-treated samples.

According to the chemical analysis results of non heat-treated zeolite and clinoptilolites treated at different temperatures and durations, it has been determined that the chemical content levels did not undergo a different change as a result of application of heat treatment.

**Table 1.** Physical analysis results of non heat-treated zeolite and clinoptilolites treated at different temperatures and durations

Analysis parameters (Ca, K <sub>2</sub> , Na <sub>2</sub> , Mg) <sub>4</sub> Al <sub>8</sub> Si <sub>40</sub> O <sub>96</sub> ·24H <sub>2</sub> O	CLP-13 NATURAL		CLP-01 300 °C 15 min		CLP-02 300 °C 30 min		CLP-03 300 °C 60 min		CLP-04 300 °C 120 min		CLP-05 450 °C 15 min		CLP-06 450 °C 30 min	
	No	No	No	No	No	No	No	No	No	No	No	No	No	No
Dispersion in the water	No	No	No	No	No	No	No	No	No	No	No	No	No	No
Fat absorption, mL/100g	38.00	32.00	31.90	32.00	31.90	32.00	36.00	36.00	44.00	44.00	42.00	42.00	45.00	45.00
Original bleaching, g sample/g tonsil	2.18	1.73	1.72	1.73	1.72	1.73	1.70	1.70	1.60	1.60	1.59	1.58	2.15	2.15
Activated bleaching, g sample/g tonsil	1.55	1.50	1.45	1.50	1.45	1.50	1.50	1.50	1.60	1.60	1.58	1.58	1.70	1.70
Water absorption capacity	18.63	25.00	20.72	25.00	20.72	25.00	22.00	22.00	27.00	27.00	30.00	30.00	20.00	20.00
Mudding and softening	No	No	No	No	No	No	No	No	No	No	No	No	No	No
Pozzolanic activity, MPa	5.65	6.70	8.36	6.70	8.36	6.70	6.30	6.30	3.30	3.30	1.20	1.20	9.70	9.70
True density, g/cm <sup>3</sup>	2.37	2.35	2.27	2.35	2.27	2.35	2.38	2.38	2.33	2.33	2.34	2.34	2.35	2.35
Apparent porosity, %	19.10	20.00	38.50	20.00	38.50	20.00	34.00	34.00	26.00	26.00	26.00	26.00	38.00	38.00
Water absorption, %	17.75	19.00	20.40	19.00	20.40	19.00	22.00	22.00	15.00	15.00	16.00	16.00	17.00	17.00
Analysis parameters (Ca, K <sub>2</sub> , Na <sub>2</sub> , Mg) <sub>4</sub> Al <sub>8</sub> Si <sub>40</sub> O <sub>96</sub> ·24H <sub>2</sub> O	CLP-07 450 °C 60 min		CLP-08 450 °C 120 min		CLP-09 600 °C 15 min		CLP-10 600 °C 30 min		CLP-11 600 °C 60 min		CLP-12 600 °C 120 min			
Dispersion in the water	No	No	No	No	Yes	Yes	No	No	No	No	No	No	Yes	Yes
Fat absorption, mL/100g	45.00	40.00	40.00	40.00	42.00	42.00	42.00	42.00	46.00	46.00	46.00	46.00	40.00	40.00
Original bleaching, g sample/g tonsil	2.16	1.65	1.65	1.65	1.65	1.65	1.63	1.63	1.69	1.69	1.69	1.69	1.55	1.55
Activated bleaching, g sample/g tonsil	1.67	1.48	1.48	1.48	1.53	1.53	1.61	1.61	1.55	1.55	1.55	1.55	1.70	1.70
Water absorption capacity	21.00	22.89	22.89	22.89	18.63	18.63	24.75	24.75	24.45	24.45	24.45	24.45	17.67	17.67
Mudding and softening	No	No	No	No	No	No	No	No	No	No	No	No	No	No
Pozzolanic activity, MPa	6.80	7.70	7.70	7.70	7.80	7.80	7.33	7.33	4.74	4.74	4.74	4.74	3.18	3.18
True density, g/cm <sup>3</sup>	2.34	2.35	2.35	2.35	2.68	2.68	2.35	2.35	2.35	2.35	2.35	2.35	2.34	2.34
Apparent porosity, %	40.00	33.00	33.00	33.00	39.10	39.10	30.12	30.12	29.62	29.62	29.62	29.62	26.14	26.14
Water absorption, %	19.00	19.00	19.00	19.00	16.00	16.00	15.73	15.73	16.55	16.55	16.55	16.55	22.00	22.00

**Table 2.** Chemical analysis results of non heat-treated zeolite and clinoptilolites treated at different temperatures and durations

Analysis parameters (Ca, K <sub>2</sub> , Na <sub>2</sub> , Mg) <sub>4</sub> Al <sub>8</sub> Si <sub>140</sub> O <sub>96</sub> ·24H <sub>2</sub> O	CLP-13 NATURA L	CLP-01 300 °C 15 min	CLP-02 300 °C 30 min	CLP-03 300°C 60 min	CLP-04 300 °C 120 min	CLP-05 450 °C 15 min	CLP-06 450 °C 30 min
<i>Chemical content, %</i>							
Na <sub>2</sub> O	0.2	0.2	0.2	0.2	0.2	0.2	0.2
MgO	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Al <sub>2</sub> O <sub>3</sub>	10.9	11.3	11.8	11.9	10.5	10.5	10.6
SiO <sub>2</sub>	72.1	68.9	68.3	68.1	69.8	69.8	69.7
K <sub>2</sub> O	3.3	3.2	2.9	2.8	3.1	3.1	3.2
P <sub>2</sub> O <sub>5</sub>	≤0.1	≤0.1	0.1	≤0.1	≤0.1	≤0.1	≤0.1
CaO	4.4	4.6	4.6	4.5	4.3	4.4	4.6
TiO <sub>2</sub>	0.1	≤0.1	0.1	0.1	0.1	0.1	≤0.1
Fe <sub>2</sub> O <sub>3</sub>	1.5	1.5	1.4	1.4	1.4	1.4	1.5
MnO	≤0.1	≤0.1	0.1	0.1	≤0.1	≤0.1	≤0.1
A.Za (1050 °C)	5.80	8.55	9.10	9.30	8.85	8.85	8.55
pH, 10%	9.32	9.40	9.40	9.20	9.47	9.40	9.32
<i>Heavy metals (mg/kg)</i>							
Cadmium	1.30	1.40	1.40	1.60	1.70	1.40	1.40
Copper	6.88	ND	ND	ND	ND	51.40	51.60
Nickel	23.88	ND	ND	ND	ND	ND	ND
Lead	50.90	51.20	51.60	51.60	52.30	ND	ND
Zinc	58.37	ND	ND	ND	ND	2.10	2.50
Mercury	ND	ND	ND	ND	ND	ND	ND
CEC, meq/g	1.60	1.80	2.50	2.60	2.20	2.10	2.50
Clinoptilolite, %	95	-	-	-	-	-	-
Feldspar, %	3	-	-	-	-	-	-
Mica, clay, lead, fibrous structure and quartz	No	-	-	-	-	-	-
Dioxin (ng/kg)	0.2	ND	ND	ND	ND	ND	ND

ND – not detected.

**Table 2 (cont'd).** Chemical analysis results of non heat-treated zeolite and clinoptilolites treated at different temperatures and durations

Analysis parameters (Ca, K <sub>2</sub> , Na <sub>2</sub> , Mg) <sub>4</sub> Al <sub>8</sub> Si <sub>40</sub> O <sub>96</sub> ·24H <sub>2</sub> O	CLP-07 450 °C 60 min	CLP-08 450 °C 120 min	CLP-09 600 °C 15 min	CLP-10 600 °C 30 min	CLP-11 600 °C 60 min	CLP-12 600 °C 120 min
<i>Chemical content, %</i>						
Na <sub>2</sub> O	0.2	0.2	0.2	0.2	0.2	0.2
MgO	1.1	1.1	1.1	1.1	1.1	1.1
Al <sub>2</sub> O <sub>3</sub>	10.6	10.7	10.6	10.6	10.6	10.7
SiO <sub>2</sub>	70.0	68.1	70.5	70.1	70.4	70.7
K <sub>2</sub> O	3.2	3.2	3.2	3.2	2.9	3.2
P <sub>2</sub> O <sub>5</sub>	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1
CaO	4.3	4.2	4.4	4.6	4.2	4.2
TiO <sub>2</sub>	0.1	0.1	0.1	≤0.1	0.1	0.1
Fe <sub>2</sub> O <sub>3</sub>	1.5	1.4	1.5	1.5	1.5	1.4
MnO	0.1	0.1	≤0.1	≤0.1	0.1	0.1
A.Za (1050 °C)	9.10	7.85	7.80	7.95	8.25	7.65
pH <sub>3</sub> , 10%	8.60	8.75	8.73	9.20	9.20	9.11
<i>Heavy metals (mg/kg)</i>						
Cadmium	<0.1	1.70	1.50	1.50	1.70	1.90
Copper	69.73	52.30	ND	ND	ND	ND
Nickel	65.76	ND	ND	ND	ND	ND
Lead	<0.05	ND	52.20	52.20	52.80	53.70
Zinc	2.70	2.20	ND	ND	ND	ND
Mercury	ND	ND	ND	ND	ND	ND
CEC, meq/g	2.70	2.20	2.00	2.10	2.10	2.00
Clinoptilolite, %	-	-	-	-	-	-
Feldspar, %	-	-	-	-	-	-
Mica, clay, lead, fibrous structure and quartz	-	-	-	-	-	-
Dioxin (ng/kg)	ND	ND	ND	ND	ND	ND

ND – not detected.

Only A.Za ( 1050 °C) level was at the level of 5.80 in non heat-treated natural CLP 13 while it was determined as 8.55, 9.10, 9.30, 8.85, 8.85, 8.55, 9.10, 7.85, 7.80, 7.95, 8.25 and 7.65, respectively in heat-treated samples. Cadmium level was at the level of 1.30 mg/kg in non heat-treated natural CLP 13, while it increased with heat treatment in all samples except CLP 07 – 450 °C/ 60 mins. Copper was found at the level of 6.88 mg/kg in non heat-treated natural CLP 13, while it was not found in treated samples of CLP 01 – 300 °C/15 min, CLP 02 – 300 °C/30 min, CLP 03 – 300 °C/60 min, CLP 09 – 600 °C/15 min, CLP 10 – 600 °C/30 min, CLP 11 – 600 °C/ 60 min, CLP 12 – 600 °C/120 min. In treated samples of CLP 05 – 450 °C/15 min, CLP 06 – 450 °C/30 min, CLP 07 – 450 °C/60 min, CLP 08 – 450 °C/120 min, copper ratio was respectively at the level of 51.40 mg/kg, 51.60 mg/kg, 69.73 mg/kg and 52.30 mg/kg, respectively. Nickel level was 23.88 mg/kg in non heat-treated natural CLP 13 and 65.76 mg/kg in CLP 07 – 450 °C/60 min treated samples while it was not found in any of the other samples.

Lead level was at the level of 50.90 mg/kg in non heat-treated natural CLP 13 while it was determined as 51.20, 51.60, 51.60, 52.30, 0.00, 0.00, <0.05, 0.00, 52.20, 52.20, 52.80, 53.70, respectively in heat-treated samples. Accordingly, lead could not be detected in the samples which underwent heat treatment at 450 °C. Zinc level was 58.37 mg/kg in non heat-treated natural CLP 13, while it was determined as 2.10, 2.50, 2.70, 2.20 mg/kg in treated samples of CLP 05 – 450 °C/15 min, CLP 06 – 450 °C/30 min, CLP 07 – 450 °C/60 min, CLP 08 – 450 °C/120 min, respectively. It has been found that the non heat-treated natural CLP 13 with a cation exchange capacity (CEC) of 1.60

meq/g increases this value with different duration and heat treatment. The highest levels were determined as 2.60 and 2.70 meq/g in samples of CLP 03 – 300 °C/60 min and CLP 07 – 450 °C/60 min. Mineral content examination was carried out only on non heat-treated natural CLP 13, and the % level of clinoptilolite was determined as 95% while the level of feldspar was determined as 3%. Dioxin analysis was carried out on all samples used in the study; dioxin level was at the level of 0.2 ng/g in non heat-treated natural CLP 13, while it was not found in any of the heat-treated samples.

## DISCUSSION

Adsorption process is under the influence of many physico-chemical factors such as surface area of adsorbent, particle size, temperature, pH and contact time (Kılıç *et al.*, 2005). The adsorption criteria of the substances used as adsorbent can be increased by using some physical and chemical processes. A total of 13 trial samples consisting of one control (non heat-treated) and 12 trial groups, in which 3 different temperatures (300 °C, 450 °C and 600 °C) and 4 different heating durations (15 min, 30 min, 60 min, 120 min) were applied, were analysed in terms of physicochemical properties, and mineral content and chemical content as well as physical properties were determined through X-ray diffraction method, XRF Spectrophotometer and analyses, respectively. The most important property of zeolites is that its honey pectin-like micropores are filled with water at room temperature. It is stated that adsorption amount of zeolites can also be increased due to the pores left by water that evaporates when heated at 350–400 °C. There are three types of water in clinoptilolite; namely free-water, lightly bound water

and tightly bound water. Knowlton & White showed in their studies that free water can be removed from the structure at 65–85 °C, lightly bound water at 171 °C and tightly bound water at 271 °C. They explained that there was no deterioration in the crystal structure, and the reason for this was that the thermal stability of clinoptilolite was not about 700 °C (Ülkü *et al.*, 1999).

The studies carried out have mostly focused on the absorbing effects of clinoptilolites on heavy metals in the water. In addition, it has been found that heat treatment application on clinoptilolites and duration of the application have effects on physical properties. Adsorption reactions vary by the endothermic or exothermic nature of the temperature. In many reactions, it is usually stated that the reaction speed increases when the temperature increases. Temperature is a significant criterion in adsorption process and affects the adsorption speed (Duman, 2012). In fact, similar to findings in this study, Yavuz *et al.* (2003) carried out studies to separate the heavy metals Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solutions by using kaolinite, and measured their kinetic and thermodynamic parameters ( $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ ). As a result, they have showed that adsorption is an endothermic reaction and metal adsorption is faster at high temperatures. Celebi *et al.* (2005) used clinoptilolite in refinement of waste water containing Ni (II). In the study, synthetic waste water consisting of nickel ion was used, and effects of parameters such as time, pH, concentration and adsorbent amount on adsorption were investigated. Maximum removal efficiency was achieved in 30 min and at pH 6 as 98%.

As a result of this study, it has been demonstrated that heat treatment applica-

tion does not undergo any change in the chemical content of clinoptilolite. However, especially contents of Cd and Pb, among the heavy metals, significantly decreased as a result of 450 °C and 60 min heat treatment. Heat treatment at higher temperatures or durations showed no effect on heavy metals. This situation shows that heat treatment can eliminate the inconveniences that may arise from consideration of clinoptilolites as toxin binders.

## CONCLUSION

Consequently, it has been observed in the pre-heat treatment trials carried out by means of different methods that the adsorption level of clinoptilolite which is non heat-treated, only subjected to acid treatment with micronisation, was 200–400 m<sup>2</sup>/g, while this level can reach up to 900–1200 m<sup>2</sup>/g in clinoptilolite that is highly activated by treating it at different temperatures and durations. Therefore, it can be stated that micotoxins, moisture and gas binding capacity of clinoptilolite can increase about 4 times compared to clinoptilolite produced by means of conventional method. In addition, the application of heat treatment will reduce the proportion of some heavy metals available in the structure of clinoptilolites, and eliminate the possible negative effects. It is considered that studies should be carried out to investigate the effects of feeds, in which clinoptilolites, adsorption properties of which are increased by heat treatment, are used as toxin binders on animals, and the positive effects thereof should be revealed.

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