

## Control of Odorants Emissions from Poultry Manure Using Jordanian Natural Zeolites

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### ABSTRACT

Natural zeolitic tuffs from Tall Juhira (southern Jordan) have been investigated and tested for their odor removal capacity. Two types of Tall Juhira zeolitic tuffs were used in the odor sorption from animal wastes. The first type is the separated size fraction between 1 and 0.7 mm (TJ1), while the second type is the separated size fraction between 0.7 and 0.3 mm (TJ2). The effect of particle size was examined in the removal experiments. The main species identified in Tall Juhira natural zeolitic tuffs are: chabazite and – subordinately- faujasite and phillipsite.

Zeolitic tuff trap and batch tests were performed to determine the effectiveness of Tall Juhira zeolitic tuffs in the reduction of the odor emission from natural broiler manure. The results were interpreted by using percentage removal curves and diagrams. By using TJ1 in zeolitic trap experiments, the removal percentages of NH<sub>3</sub> ranged from 93 to 71, while by using TJ2 the removal percentages ranged from 96 to 81. In batch experiments, the use of TJ2 type shows a higher percentage of NH<sub>3</sub> retention than TJ1 type for the same time. The odor panel results show that the control manure (untreated) has the highest odor intensity in all trails. In summary, it can be concluded that odor emission from animal waste can be effectively reduced using Juhira zeolitic tuffs.

**KEYWORDS:** Zeolite, Tall Juhira, Zeolitic tuff, Broiler manure, Phillipsite, Chabazite, Faujasite, Animal waste, Odor.

### INTRODUCTION

Odor is a major problem confronting livestock producers (National Research Council, 2003). The anaerobic nature of manure stabilization can cause offensive odors and release ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), along with various Volatile Organic Compounds (VOCs) during the different stages of

animal waste handling (Bicudo et al., 2002). The semi-fluid droppings in large poultry houses emit a stench that is discomforting to farm workers and to the chickens themselves. The noxious fumes of ammonia contribute to decreased resistance to respiratory diseases, resulting in smaller and less healthy birds (Kling and Quarles, 1974) and decreased egg production (Change and Flint, 1976). Odor complaints have been registered with increasing frequency by nearby residents or neighboring businesspeople as well as by travelers.

Odor control has proved to be technologically

difficult to achieve (Miner, 1983). However, several studies show that the environmental problems associated with poultry manure could be mitigated using

natural zeolites (McCroly and Hobbs, 2001; Mumpton and Fishman, 1977).

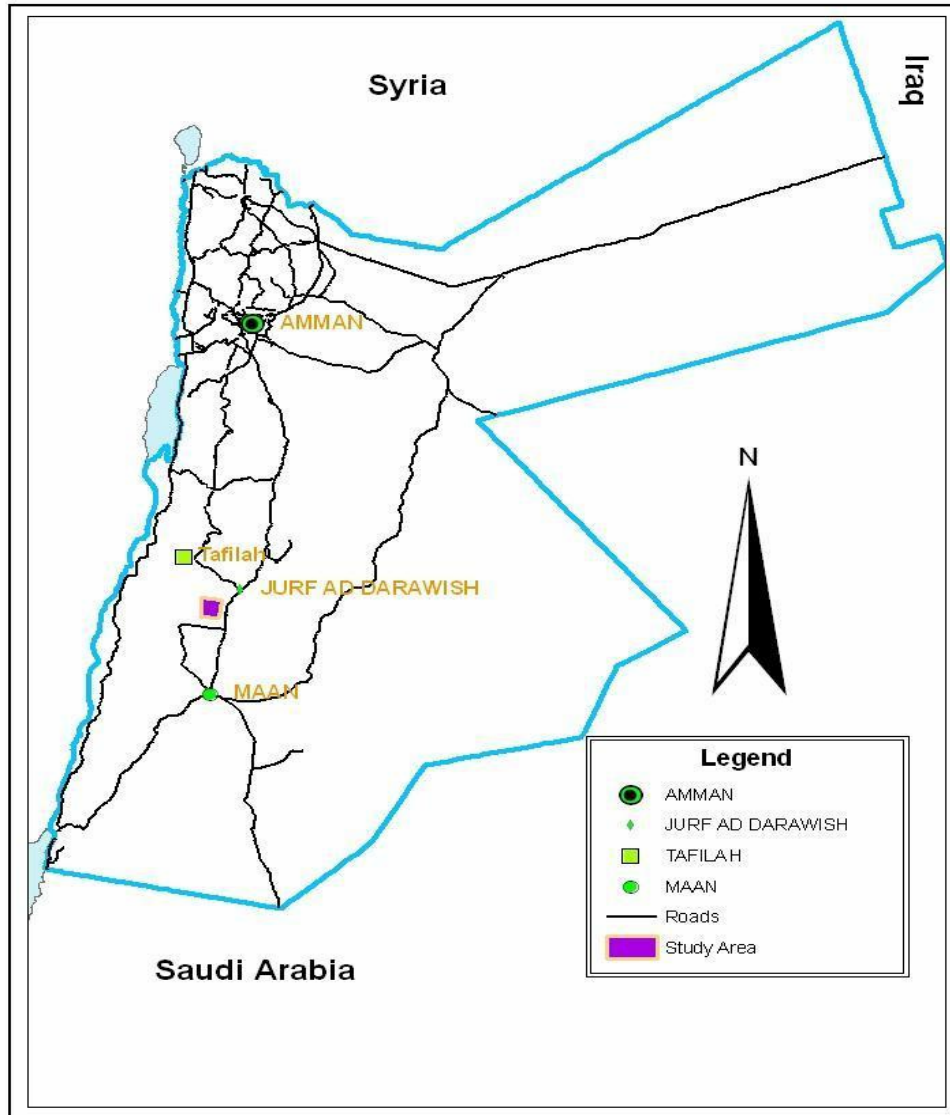


Figure 1: A location map showing Tall Juhira volcano in south Jordan

Zeolites are a group of hydrated aluminum-silicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium) characterized by low mining cost, availability, bulk density and high resistance to alteration (Mercer and Ames, 1978).

Zeolites have a three-dimensional crystalline framework of tetrahedral silica or alumina anions strongly bonded at all corners, and they contain channels filled with water and exchangeable cations.

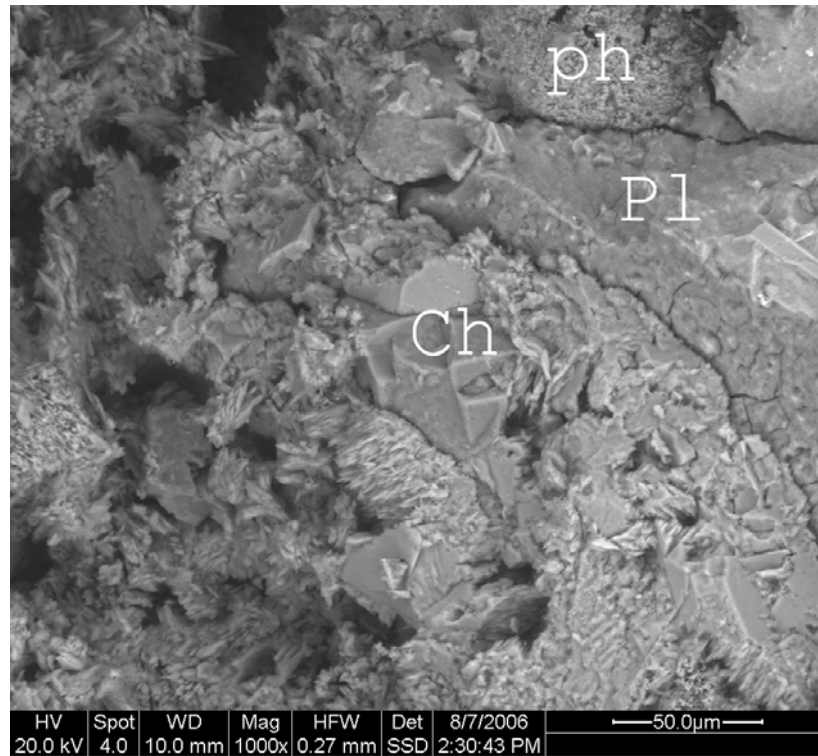


Figure 2: Scanning electron micrographs of zeolitic tuff samples from Tall Juhira showing zeolitic mineral crystals (chabazite and phillipsite)

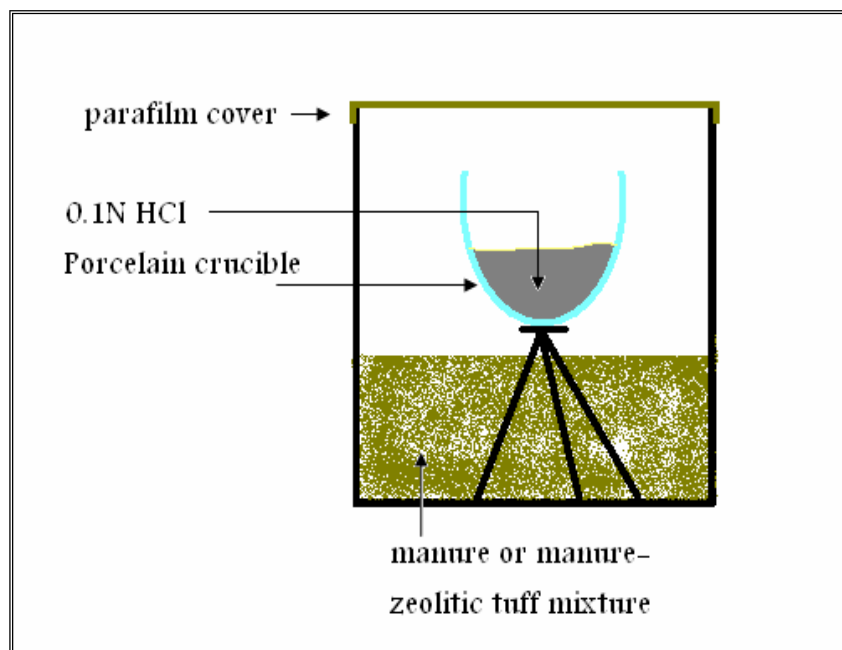


Figure 3: Schematic diagram illustrating the methodology used to collect the ammonia released from broiler manure or manure/zeolitic tuff mixtures

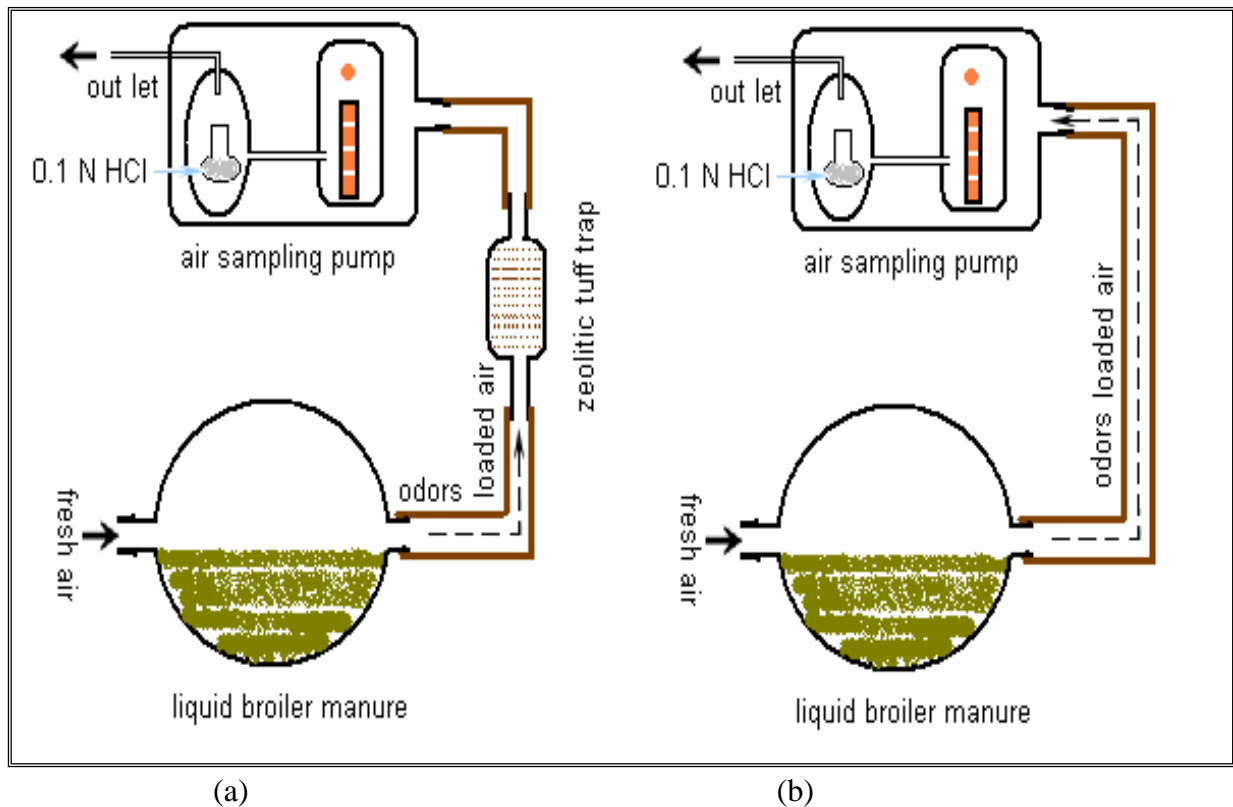


Figure 4: Air purification system showing the liquid broiler manure flask, zeolitic tuff trap and air sampling pump

The structure is suitable for ion exchange due to isomorphism: the replacement of  $Al^{3+}$  with  $Si^{4+}$  in the structure, giving rise to a deficiency of positive charge in the framework. This is balanced by mono and divalent exchangeable cations such as  $Na^+$ ,  $Ca^{2+}$ ,  $K^+$  and  $Mg^{2+}$ . The main consequence of this structure type is represented by the reversibility of hydration and cation exchange processes that preserve the original network. Thus, they present specific properties (e.g., adsorption-desorption capacity, ion exchange capacity, catalytic properties), which confer to this group of minerals important and diverse possibilities of usage.

Ion exchange capacity and cation selectivity are the most important properties for zeolite as a natural molecular sieve material for wastewater treatment. Ion exchange was defined as a process where an insoluble substance removes ions of positive or negative charge

from an electrolytic solution and releases other ions of similar charge into the solution in a chemically equivalent amount (Benfield, 1982). Cation selectivity refers to the preference order of zeolite for cations based on the various factors which determine the selectivity. Ion size, valence and hydration energies are important factors in determining the selectivity of a given ion in a specific system. The zeolite prefers or is more selective for certain cations and less selective for others (Colella, 1996). Mercer *et al.* (1970) have used natural zeolite to remove ammonium ions from wastewater. Simes and Hindin (1978) have demonstrated that the preferred method for removing traces of  $NH_4^+$  from fresh hatchery water is a possible method to satisfy the standard for water reuse. The proposed design has used an ion exchange using natural clinoptilolite. Blanchard *et al.* (1984) have indicated that clinoptilolite has a

good selectivity for the ammonium ion. The efficiency order is as follows:



The above-mentioned heavy metals- as well as ammonium in wastewater-can be treated by being passed through clinoptilolite columns. Semmens (1978) suggested that clinoptilolite is highly selective for barium and lead, but less selective for copper, cadmium and zinc.

Zeolites in Jordan were first discovered by Dwairi (Dwairi, 1987). The Jordanian phillipsitic tuff has a good efficiency in ammonium removal from wastewater, as good as Hungarian clinoptilolite, but phillipsite is more selective for ammonium ions (Dwairi, 1991). In addition, Dwairi (1992) found that the Jordanian phillipsite is of good efficiency for cesium fixation and immobilization from nuclear waste in comparison with phillipsitic rich tuff from California and moderate rich tuffs from Arizona and Nevada. Al-Sharadqah (1994) evaluated the Jordanian phillipsitic zeolitic tuff from Jabal Aritayn in animal waste treatment and enhancement of their characteristics as natural fertilizers. Ed-Deen (1998) evaluated zeolites from Tell Rimah for industrial wastewater treatment. The results have indicated that Tell Rimah zeolitic tuff showed high selectivity for the removal of Cu, Cr, Ni and Zn from Electroplating Factory effluents and could be used for removing Pb and Fe from the wastewater of the Battery Factory. Al-Dwairi (2007) studied the characterization of Jordanian zeolitic tuff and its potential use in wastewater treatment. He studied the mineralogy and geochemistry of all zeolitic tuff localities in Jordan and evaluated Jordanian natural zeolitic tuffs obtained from Hannoun (HNZ) and Mukawir (MNZ) volcanoes for removing selected heavy metals (Zn and Pb) and total organic carbon from domestic wastewater. The results showed that the main zeolite minerals are: phillipsite, chabazite, faujasite and analcime. The environmental experiments showed that HNZ and MNZ are suitable for domestic wastewater treatment. Ibrahim and Jbara (2009) used natural phillipsite-faujasite tuff from Jordan to remove paraquat

from synthetic wastewater. They found that natural zeolites are suitable to remove paraquat.

Al Dwairi (2009) evaluated the Jordanian phillipsitic tuff from Al-Ataita volcano for applications in wastewater treatment. He concluded that Al-Ataita phillipsitic tuff shows good removal percentages of ammonium from municipal wastewater. Al-Dwairi (2010) used southern Jordanian zeolitic tuffs (Jabal Uniza) as pollutant control in removing heavy metals from industrial wastewater plants. He concluded that Jabal Uniza zeolitic tuff has a good removal percentage of heavy metals (Cd and Mn) from industrial wastewater.

Southern Jordan volcanic eruptions consist of many volcanic cones. Tall Juhira volcano is one of these cones. It lies about 175 km south of Amman as shown in Figure 1 with a height of 1144m above the sea level (Ibrahim, 1987). Lithologically, Tall Juhira volcanic rocks are 110 meters thick and comprise well bedded lapilli and ash. The dominating zeolites in Tall Juhira zeolitic tuff are chabazite as the major mineral and phillipsite and faujasite as minor minerals (Al-Dwairi, 2007) (Fig. 2). Because of the accessibility to huge amounts of zeolitic tuff close to the highway leading to Aqaba, this location has been chosen from among the southern Jordanian zeolitic tuff locations to be used as pollutant control in removing odor from animal wastes. This location has not been studied before for its industrial or environmental application.

## MATERIALS AND METHODS

Two types of zeolitic tuffs were used in the experiments; Tall Juhira processed sample (TJ1) and Tall Juhira processed sample (TJ2). A bulk sample of nearly fresh broiler manure was collected from the storage tank of a broiler poultry farm in Irbid area. Two systems of experiments were carried out: zeolitic trap experiments and zeolitic batch experiments.

### Samples Preparation

Tall Juhira chabazitic tuff bulk sample (TJ) was

collected as channel sample and crushed using a crusher with an aperture of 5 cm and sieved into two sizes; TJ1 (1-0.7 mm) and TJ2 (0.7-0.3 mm). Tall Juhailra zeolitic content was determined by Al-Dwairi (2007), who found that fractions between 1 and 0.3mm have the highest zeolitic content (75%). Natural zeolitic tuff samples were used in the removal experiment without any modification or chemical treatment. Broiler manure used in all experiments was obtained as a bulk sample (30 liters) from a poultry farm. The sample was divided into two representative samples to be used in odor removal experiments. The first part was used directly in the batch experiments, while the second one was stored under anaerobic conditions to be used in the zeolitic tuff trap experiments.

## EXPERIMENTAL METHODS

### A. Experiment One (Batch Method)

Three replicates of 150 cm<sup>3</sup> of fresh broiler manure were prepared. The first one was mixed with 75 cm<sup>3</sup> of TJ1 zeolitic tuff in a 500cm<sup>3</sup> plastic beaker. The second one was exactly the same except that the zeolitic tuff size was TJ2. The third replicate was the control sample (no zeolitic tuff has been added).

The omitted NH<sub>3</sub> and overall odor intensity were evaluated using two procedures; HCl trap and odor panel. In the first procedure, a porcelain crucible containing 10ml of 0.1N HCl was placed over a tripod stand 20mm over the surface of the manure – zeolitic tuff mixture or over the manure sample in the case of control sample (Fig. 3). Each beaker was closed by multilayeres of parafilm for 24 hours. Then the cover was removed to replace the crucible by a new one containing 10ml of 0.1N HCl. The same process was repeated 5 times (five days). The released NH<sub>3</sub> by manure was estimated by analyzing the HCl solution for its NH<sub>3</sub> content using nesslerization.

In the second procedure, the overall odor intensity was estimated comparatively by a 3 member odor panel. Each member has sniffed the three beakers one after one immediately after removing the parafilm covers, then

the member classified the odor intensity or the beaker relatively. The highest odor intensity was assigned the maximum value (3), the moderate odor intensity the value (2) and the minimum odor intensity the lowest value (1). The overall odor intensity for each treatment was evaluated as the summation of the three assignments.

### B. Experiment Two (Zeolitic Tuff Trap)

This experiment aimed at purifying the air from odors released by manure. A stored sample of liquid manure under anaerobic conditions for 2 weeks was selected for this experiment. The bulk sample of 1350 cm<sup>3</sup> was poured into three spherical flasks of 1100 cm<sup>3</sup> (Fig. 4). the first two flasks were connected to 40 cm<sup>3</sup> traps filled by zeolitic tuff. The grain size of zeolitic tuff ranged from 1.0-0.7 mm (TJ1) in the first trap and 0.7-0.3 mm (TJ2) in the second one. For air sampling, a pump was connected to the zeolitic tuff trap (Fig. 4a) or directly to the spherical flask in the case of the control sample (Fig.4b).

When the pump was turned on, it sucked the fresh air through the manure flask, then passed it through the zeolitic trap or directly to the sampling pump in the case of the control sample. Within the sampling machine, the passed air was percolated in 0.1N HCl solution to dissolve ammonia and methylamine escaping the zeolitic tuff trap.

The volume of the air sample passed through the system was ten liters at a rate of 0.5 l/minute. Two daily air samples were taken for fifteen days. The ammonia concentration of the absorbing solution (0.1N HCl) was measured by nesslerization .

## RESULTS AND DISCUSSION

### Results of Batch Experiments

The results of batch experiment adsorption are listed in Table (1) and represented in Figure (5). The data in Table 1 represent the amount of ammonia released by manure every day. The data show that the control

manure sample emits more ammonia than the other two samples in all trials, while the manure- TJ2 mixture emits less ammonia in all trials. It can also be observed from Table 1 that the cumulative concentration of  $\text{NH}_3$  released from manure in 5 days of the experiment has decreased from 2.6 (mg) for the control sample to 1.26 and 0.73 for the mixture of manure and zeolitic tuff fractions TJ1 and TJ2, respectively. Figure 5 shows the percentage of reduction of  $\text{NH}_3$  from manure using different sizes of chabazitic tuff. The Figure shows that the removal percentage for ammonia ranges between 60 and 80% using TJ2, and between 32 and 57% using TJ1.

**Table 1:  $\text{NH}_3$  concentration in the absorbing solution of the batch experiment**

Trial # (Day)	Concentration of $\text{NH}_3$ released by manure (mg/day)		
	Control	Manure-TJ1 mixture	Manure TJ2 mixture
1	0.4	0.27	0.15
2	0.16	0.07	0.06
3	0.27	0.13	0.11
4	0.94	0.43	0.24
5	0.83	0.36	0.17
Accumulative $\text{NH}_3$ (mg)	2.6	1.26	0.73

The results of the second procedure (odor panel) are presented in Fig. 6. The results show that the control sample has the highest odor intensity in all trials, while the manure TJ2 has the lowest odor intensity in all trials. However, one member of the odor panel was assigned a higher intensity odor value for manure- TJ2 in the second day of the experiment. The results obtained from this procedure agree with the results of the first one. TJ2 has more efficiency in ammonia removal and odor control. This is probably due to the higher percentage of zeolitic minerals in the finer fractions.

**Table 2:  $\text{NH}_3$  concentration in the air samples as measured in the absorbing solution**

Air sample		System		
Day	Air sample #	Control	TJ1-Trap	TJ2-Trap
1	1	211	13	9
	2	187	12	11
2	3	322	32	21
	4	296	29	22
3	5	228	31	17
	6	188	24	19
4	7	432	25	22
	8	378	29	24
5	9	545	44	31
	10	565	59	45
6	11	455	55	32
	12	466	44	31
7	13	322	49	29
	14	412	46	31
8	15	266	33	25
	16	322	37	22
9	17	543	44	29
	18	487	65	33
10	19	452	61	29
	20	472	59	27
11	21	311	32	22
	22	255	32	23
12	23	166	22	19
	24	132	19	21
13	25	154	25	19
	26	109	22	14
14	27	101	19	17
	28	123	22	18
15	29	77	17	11
	30	64	18	12
Average $\text{NH}_3$ concentration		301	34.5	23

The results obtained by the present experiment closely agree with the results obtained by Lingshuang et al. (2007) and Onagi (1965). The overall odor intensity

reduction is partially due to effective ammonia removal. It is also expected that zeolites because of their properties could effectively adsorb VOCs and other

odorous compounds as suggested by Lingshuang et al. (2007).

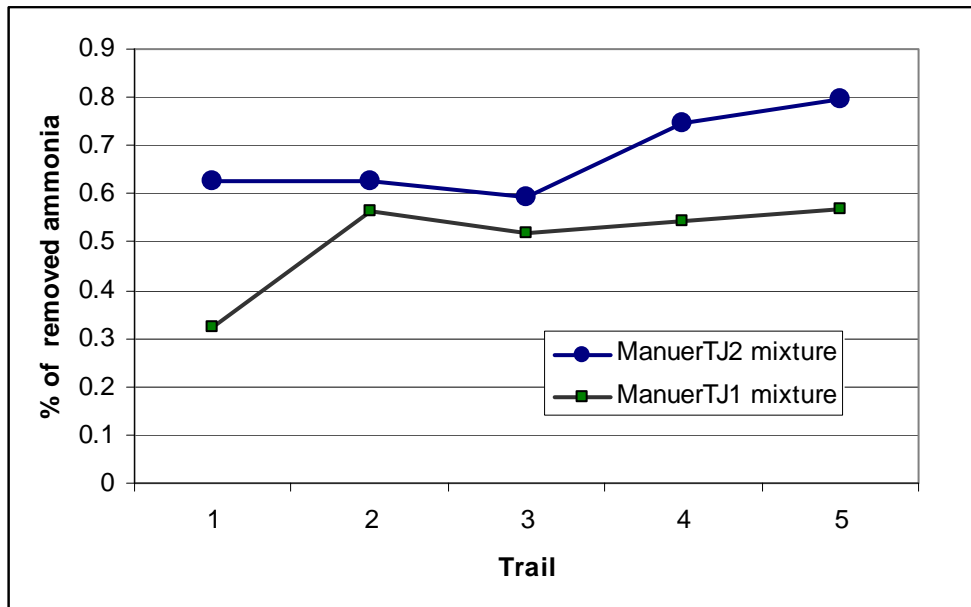


Figure 5: Ammonia concentration in the absorbing solution of batch experiment

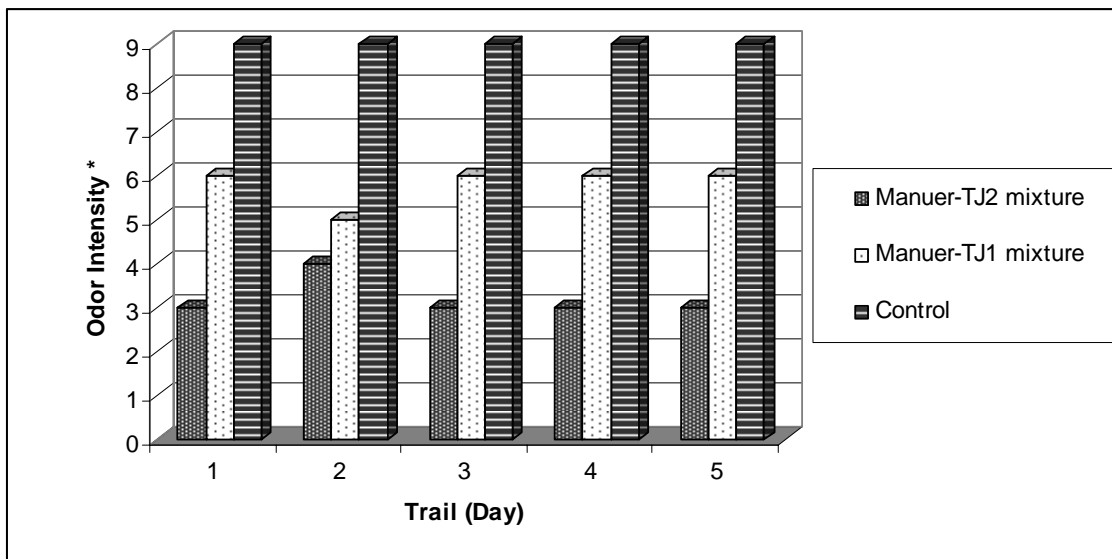
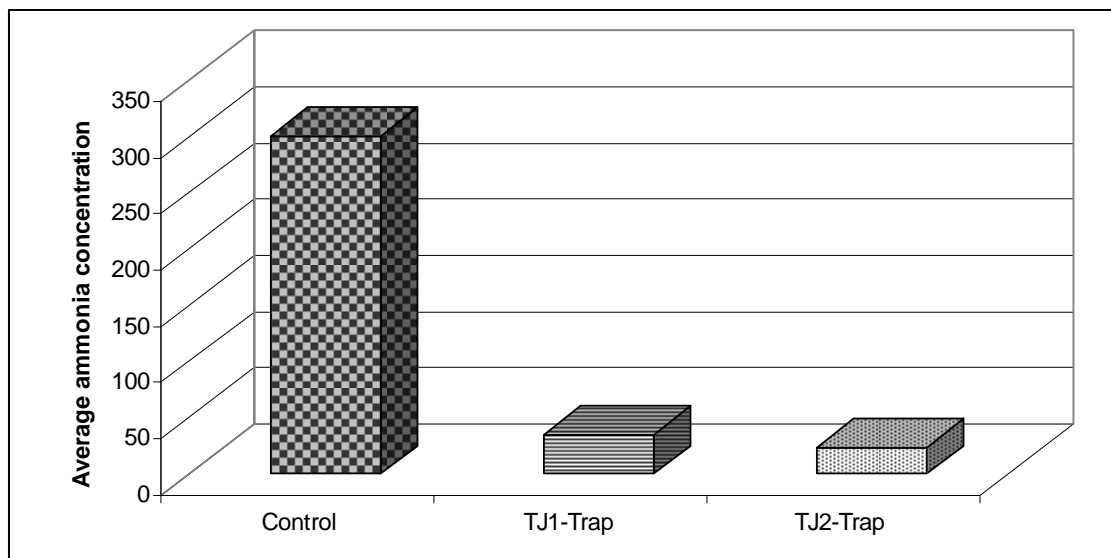


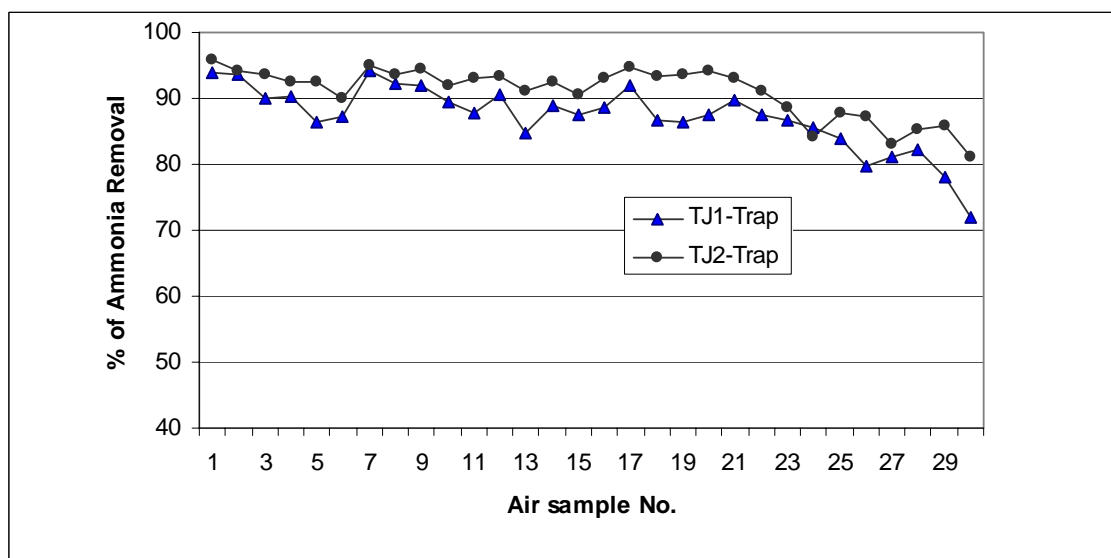
Figure 6: Odor intensity as assigned by the three members of the panel for a control manure sample and two manure-zeolitic tuff mixtures

(\*): The given odor intensity is represented by the accumulative odor intensities as assigned by the three member panel. Each member is assigned a value for each treatment depending on its odor intensity: For maximum intensity the assigned value is 3, for moderate intensity 2 and for minimum intensity 1.





**Figure 7: Average concentration ammonia escaping from zeolitic tuff traps or directly from manure in the case of control sample**



**Figure 8: Percentage removal of ammonia using different grain sizes of Tall Juhira zeolitic tuff**

### Results of Zeolitic Tuff Trap Experiment

The zeolitic tuff trap experiment was carried out using the two types of zeolitic tuff (TJ1 and TJ2). The results of the experiment are listed in Table 2 and illustrated in Figures 7 and 8. The results demonstrate that ammonia concentration in air samples released

directly from control manure samples was the highest in all trials (Table 2). The average concentration of  $\text{NH}_3$  escaping from the manure control sample as measured in the absorbing solution is 301mg, while what escaped from the zeolitic tuff trap was 34.5 and 23 mg from TJ1 and TJ2, respectively. Figure 8 shows that 93 to 71%

and 96 to 81% of ammonia released by manure was removed by passing the zeolitic tuff traps TJ1 and TJ2, respectively.

The results of zeolitic tuff traps show that TJ2 is able to remove more ammonia than TJ1. This result agrees with the batch experiment and also could be due to higher zeolitic content in TJ2 fractions. The results agree with those of Koelliker et al. (1980). However, the maximum obtained removal percentage of ammonia was 45%. The higher percentage of ammonia removal achieved in this experiment could be attributed to higher contact time.

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### CONCLUSION

Experimental data have revealed that Jordanian natural zeolitic tuff (TJ1 and TJ2) is effective for the removal of ammonia and the control of odor emission from poultry manure, either in form of zeolitic tuff traps or by simply mixing the zeolitic tuff with the animal waste.

Zeolitic tuff fractions TJ2 are more effective than TJ1 in absorbing ammonia and other odorants nearly in all trials of both experiments.

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