

Effect of Iranian Natural Zeolite on Poultry Litter Paperboard Properties

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This study was carried out to examine the effects of Iranian natural zeolite application to poultry litter paperboard. To examine the effect of different amounts of zeolite on poultry litter paperboard's properties, four levels of zeolite were used: 0 (control), 8.85, 14.77, and 22.34%. The results showed that zeolites had significant effects on the physical properties of the paperboard. Increases in the amount of zeolite resulted in increases in both the thickness and apparent density and decreased the air resistance of the paperboard. Also, zeolites significantly reduced the strength properties of the paperboard. The effect of increasing the amount of zeolite on the water absorption properties of the paperboard was significant at the 95% confidence level; by increasing the amount of zeolite, the capacity and rate of water absorption of the paperboard increased significantly.

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INTRODUCTION

Zeolites are crystalline, microporous, inorganic materials that have unique light adsorption, catalysis, and ion exchange properties. Because of these properties, zeolites are used in a variety of applications, including adsorption of various liquids and harmful substances, removal of foul odors, soil improvement, and removal of ammonium ions from sewage water and wastewater. There are three types of zeolites: natural zeolites that occur naturally as minerals; synthetic zeolites which are produced industrially; and artificial zeolites that are made from ashes, such as coal ash and paper sludge ash. A key property of a number of zeolites is their ability to adsorb water (Kazemian *et al.* 2003; Polat *et al.* 2004; Brouillette *et al.* 2004).

To achieve maximum poultry production, efficient management of the poultry house environment is essential. An important measure of a suitable environment is proper maintenance of poultry litter. In poultry production, wood shavings are commonly used as a bedding material. Attempts have been made to use and test several other types of materials as litter (Villagra *et al.* 2011).

Different types of bedding material such as cotton waste, recycled paper chips from waste newspapers, particleboard residues, sand, wheat stalks, rice hull, sunflower, peanut hulls, wood shavings, wheat straw, and others are generally used as poultry litter. The use of any of these substrates most often depends on the availability and economics in each

area at the time. Several factors help to determine whether a material would be good bedding. In general, it has to be very absorbent and have a reasonable drying time and must not be toxic to the poultry or poultry farmers. Regardless of the material used, it should be water absorbent, inexpensive, readily available, without causing problems when used as manure (Jordaan 2004; Villagra *et al.* 2011).

Table 1 lists several alternative litter materials that have been used with varying degrees of success, along with their main advantages and disadvantages (revised from Ritz *et al.* 2005).

Table 1. Advantages and Disadvantages of Various Poultry Litter Materials

Materials	Advantages	Disadvantages
Pine shavings and sawdust	Preferred material with good absorbency	Limited supply and high cost in many areas
Hardwood shavings and sawdust	Readily available in some regions	High moisture content and risk of mold growth
Pine or hardwood chips and bark	Good absorbency	May increase breast blisters when wet
Rice hulls	Good absorbency and competitive price	Chicks may eat litter; limited availability
Peanut hulls	Inexpensive in peanut-producing areas	Tends to cake, susceptible to mold and aspergillosis
Crushed corn cobs	Acceptable absorbency	Limited availability and risk of breast blisters
Chopped straw, hay or corn Stover	Widely available	High tendency to cake and mold growth
Processed paper	Good absorbency and recyclable	May cake if particles are large; requires careful management

Although zeolites have been widely used in various industries, little research on employing zeolites as water absorbent agents or fillers for paper and paperboard has been reported, especially in Iran. Ichiura *et al.* (2003) considered the influence of the uniformity of zeolite sheets prepared using a papermaking technique on VOC adsorptivity and observed that the maximum adsorption capacity of the zeolite sheet depended only on the amount of zeolite in the sheet. Sain *et al.* (2000) reported that porous, inorganic compounds having a specific surface area of about 700 to 1000 m²/g can be used in an effective way for the adsorption of colloidal material. Danesh and Fonouni (2008) investigated the effect of zeolite on reducing the humidity of poultry litter compared with that of paperboard. They reported that the zeolite reduced litter moisture. Selders *et al.* (1990) showed that newspaper absorbs more water than other types of bedding such as sawdust, wood chips, and straw. Loranger and Chabot (2004) have studied the effects of zeolite addition in a fiber suspension with comparisons to PCC filler. They found that the retention of zeolite filler was very similar to PCC retention but that the zeolite filler improved the brightness of the handsheets compared to PCC-containing handsheets at the same ash level.

In most countries, the use of wood shavings is restricted due to other industrial applications and researchers have introduced various alternative materials. In Iran, wood shavings are still used as poultry litter. The development of the wood waste conversion industry and the use of these materials to make wood products (such as particleboard) and reduce wood production have reduced the supply of wood shavings. Meanwhile, the

expansion of the poultry industry has increased the demand for wood shavings and has made it necessary to replace them with other materials (Grimes *et al.* 2007; Khosravinia 2008).

Farmers continuously look for cheap, readily available litter. Recycled paper and paperboard and zeolites are cheap and readily available in Iran because Iran has great natural zeolite resources (Kazemian 2000).

The abundance of natural zeolite resources in Iran can play a great role in developing this technology. According to published results, zeolites are suitable adsorbents for different polar and nonpolar molecules including CO₂, SO₂, NO₂, NO, H₂S, NH₃, H₂O, aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, and other similar molecules. Use of natural zeolite as a sorbent has considerably increased in different industries. Adsorption, ion exchanging, and the catalytic behavior of different zeolites has made them an interesting material to different industrial and environmental applications (Asilian *et al.* 2004).

This paper presents the results obtained from a study on the effects of Iranian natural zeolite on the properties of poultry litter paperboard that was conducted by the Wood and Paper Science Lab of Gorgan University of Agricultural Science and Natural Resources.

EXPERIMENTAL

The raw material used in this study was refined mixed recycled pulp that was provided by a factory producing poultry litter paperboard in the Golestan province. The mineral material studied as an absorbent agent was Iranian natural zeolite powder that was purchased from one of the active companies supplying and selling this material in the Golestan province.

Zeolite powder was screened with an 80-mesh sieve, and the particles passing through the sieve were isolated for testing. To determine the type of zeolite mineral and its chemical constituents, X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF) were used in the Materials and Energy Research Center (MERC), Tehran, Iran.

The pulp was disintegrated at 3000 rpm for 5 min to ensure that all fibers were well-dispersed. According to standard T 227 om-99 TAPPI, the freeness of the pulp was measured. According to standard T 205 sp-02 TAPPI, 120 g/m² handsheets were prepared at different zeolite contents (0, 10, 20, and 30% based on the dry weight of the paperboard). According to standard T 211 om-02 TAPPI, the ash content of the paperboards was determined by ignition at 900 °C for 4 h. The physical properties, such as the thickness, bulk, and air resistance, as well as strength properties such as tear strength and burst strength were tested according to TAPPI standard methods. Water absorption properties such as the rate of water absorption were measured according to TAPPI standard methods (T 835 om-03), whereas other water absorption properties such as the capacity of water absorption were measured according to ISO 8787 by the KLEMM method. The effect of Iranian natural zeolite on the properties of poultry litter paperboard were analyzed using one-way ANOVA and the means were compared using Duncan's multiple comparison tests at the 95% confidence level.

RESULTS AND DISCUSSION

XRF and XRD

To characterize the elements present in the zeolite sample, X-ray fluorescence (XRF) was used. The results obtained from the chemical analysis of the sample are shown in Table 2.

Table 2. Chemical Composition of the Zeolite Sample Determined by X-Ray Fluorescence*

Component	Content (wt. %**)	Standard Error
SiO ₂	74.60	0.20
Al ₂ O ₃	12.70	0.20
CaO	3.20	0.08
K ₂ O	2.30	0.07
Na ₂ O	1.40	0.05
MgO	1.30	0.05
* Analyzed at Materials and Energy Research Center (MERC), Karaj, Iran		
** Contents of less than one percent were not reported		

To determine the type of zeolite, the X-ray diffraction method (XRD) was used. XRD results showed that the main phases identified included quartz (SiO₂) and heulandite (CaAl₂Si₇O₁₈·6H₂O). The results of the sample analysis are shown in Fig. 1.

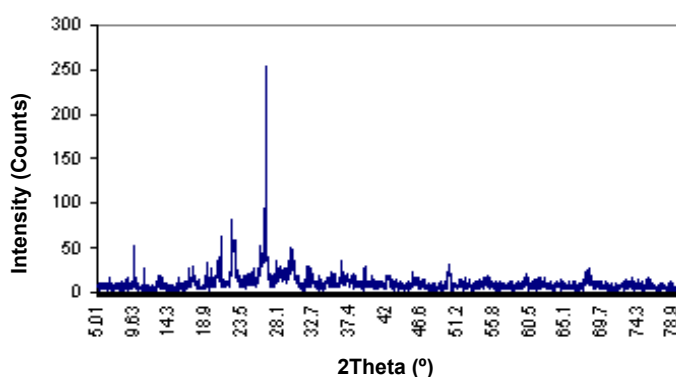


Fig. 1. XRD pattern of Iranian natural zeolite

Retention of Zeolite

Data regarding the retention of zeolite in the samples is shown in Table 3.

Table 3. Retention of Zeolite in Paperboard Samples

Treatment No.	Filler basis on pulp (%)	Filler retention (%)	Filler content (%)
1	0 (control)	0	0
2	10	85.86	8.85
3	20	74.80	14.77
4	30	75.00	22.34

Results in Table 3 suggest that zeolite is a negatively-charged particle since it was not completely (100%) retained within the fibrous matrix (Sain *et al.* 2001). The filler retention decreased with increasing filler content, but the amount of zeolite in the paperboard increased. Increasing the zeolite content in the paperboard decreased the bonding area of the fiber matrix. Thus, the ability of the matrix to retain filler decreased (Zhang *et al.* 1985).

Physical Properties

Table 4 shows the physical properties of the paperboard samples.

Table 4. Effect of Zeolite Content on the Physical Properties of Paperboard

Treatment No.	Filler basis on pulp (%)	Grammage (g/m ²)	Caliper (μm)	Bulk (cm ³ /g)	Air resistance (S)
1	0 (control)	120.6	288 ^b	2.38 ^c	9.90 ^{a*}
2	10	122.2	304 ^a	2.49 ^b	7.66 ^{ab}
3	20	122.2	314 ^a	2.56 ^a	6.23 ^b
4	30	118.7	305 ^a	2.56 ^a	5.66 ^b

* Values with different superscripts (a, b, c) within the same column are significantly different ($p < 0.05$) according to Duncan's multiple range test.

As indicated in Table 4, the caliper of the samples increased with increasing zeolite content in the paperboard. Table 4 also shows that bulk increased with increasing zeolite content in the samples. The density of fillers is usually higher than that of the fiber. Therefore, thickness increases, and a maximum thickness can be achieved at low filler content. This is not always true, as there are mineral fillers such as zeolites with particular particle shapes that can maintain or increase paper's bulk; blocky fillers increase paper thickness more than platelet-type fillers. Although particle size plays a definite role in the porosity and paper bulk, but particle size distribution and particle shape dominate the effect on paper bulk (Velho 2002). The larger particles are able to open larger inter-fiber spaces within the paper (Hubbe 2004), which contributes to the improved the bulk of paper and paperboard. This is the case when zeolites are used.

As indicated in Table 4, the air resistance of paperboards decreased with increasing amount of zeolite in the samples. Filler, especially bulky filler such as zeolites, can open sheet pores between the fibers, causing an increase in paperboard porosity's as filler loading increases. As shown in Table 4, the paperboards' porosity increased with filler content (Zhang *et al.* 1985). The influence of mineral pigment compared to that of base paper characteristics is more pronounced in terms of air permeability than paper bulk (Santos *et al.* 2000). Zeolite can pass air through its molecular sieves due to their pore structure (Wajima *et al.* 2008).

Strength Properties

Table 5 shows the strength properties of the samples. The changes in the strength properties of paperboards with different zeolite levels are shown in Table 5. It can be seen that tear strength index decreased as zeolite content increased. This can be explained by fewer fibers being available in the paperboard, since tear strength depends mainly on fiber length and bonding (Zhang *et al.* 1985). However, this decrease in tear index was very small. The tear index dropped to 36.9 mN.m²/g at 30% zeolite, representing only a 4.38% decrease compared to the control tear index (38.6 mN.m²/g).

Table 5. Effect of Zeolite Content on the Strength Properties of Paperboard

Treatment No.	Filler basis on pulp (%)	Tear index (mN.m ² /g)	Burst index (kPa.m ² /g)
1	0 (control)	38.6 ^{a *}	1.53 ^a
2	10	38.3 ^{ab}	1.22 ^b
3	20	37.7 ^b	1.02 ^c
4	30	36.9 ^c	0.99 ^c

* Values with different superscripts (a, b, c) within the same column are significantly different ($p < 0.05$) according to Duncan's multiple range test.

The influence of zeolite levels on the burst index are indicated in Table 5. The burst strength index decreased with increasing zeolite content. Such reduction of strength properties with increasing filler content is a well-known phenomenon. Fiber bonding interference increases with increased zeolite content (Loranger and Chabot 2004; Maloney *et al.* 2005). However, it seems that the zeolite has a less detrimental effect on strength properties, especially tear index, which is one positive zeolite property as compared to other materials.

Water Absorption Properties

Table 6 shows the influence of zeolite content on the water absorption properties of paperboards.

Table 6. Effect of Zeolite Content on Water Absorption Properties of Paperboard

Treatment No.	Filler basis on pulp (%)	Water absorption capacity (mm)	Water absorption time (s)
1	0 (control)	58.3 ^c	4.14 ^{a *}
2	10	68.7 ^b	2.82 ^b
3	20	74.3 ^b	2.70 ^b
4	30	84.0 ^a	1.95 ^c

* Values with different superscripts (a, b, c) within the same column are significantly different ($p < 0.05$) according to Duncan's multiple range test.

The absorbency is measured as an absorption capacity and an absorption rate. The absorption capacity is the total water absorbed by the product and absorption rate is the measurement of how fast the product absorbs water. Therefore, a product with higher water absorption capacity in a shorter period of time would be more desirable (Uner 2009).

Factors that influence water absorption capacity and water absorption time can be categorized into three groups. The first includes factors related to the sheet (capillary structure, dimensions, *etc.*); the second includes factors related to the liquid (viscosity, surface tension, *etc.*); and the third contains process conditions (temperature, pressure, *etc.*) (Shepherd and Xiao 1999; Fabritius 2007; Uner 2009). The ability of cellulosic fibers to absorb a fluid quickly depends upon having a high capillary pressure to be able to suck the liquid in and high permeability to allow the fluid to quickly flow away from the point of paper and paperboard (Beuther *et al.* 2010). The most important factors that influence the water absorption rate are the capillary force due to the pores of the sheet, inter-fiber bonding, the formation of the sheet, and the amount of pores in the sheet. Other important factors that influence the water absorption capacity are the capillary and osmotic forces present in the sheet. A cellulosic product has a specific capillary force and pore volume.

Thus, the absorption of more water can be achieved with increases in the capillary force, the osmotic force, and pore volume (Rezai and Warner 1997).

Based on the data in Table 6, the addition of zeolite improved the water absorption capacity of paperboard. Although the fibrous network of paper is complex, the liquid penetration rate into porous media can be modeled based on the Lucas–Washburn theory as follows,

$$\frac{dl}{dt} = \frac{r\delta\cos\theta}{4\mu l} \quad (1)$$

where l is the liquid penetration depth, r is the pore radius, θ is the contact angle, δ is the surface tension, and μ is the liquid viscosity. Accordingly, assuming that other factors are constant, an increase in r or a decrease in θ enhances the absorption rate ($dl:dt$). Therefore, an effective absorbent agent should either increase pore size, reduce contact angle, or both. In other words, the reduction in water absorption time can be attributed to increased fiber hydrophilicity, increased pore size, or a combination of both (Shepherd and Xiao 1999; Revised from Yoon 2007). In fact, one of the most important factors of zeolite absorbent in comparison to other mineral fillers (at the same particle size), is high specific surface of these minerals, that is due to the porous structure of the materials (Ivanov *et al.* 1997).

According to the points mentioned above, the highest zeolite content in treatment No. 4 resulted in the maximum bulk and the shortest water absorption time, indicating the highest absorption rate. Therefore, it can be concluded that zeolite addition promotes the formation of a more porous and bulkier structure in paperboard. Thus, this factor can further increase the rate of water absorption in paperboards (Ivanov *et al.* 1997).

CONCLUSIONS

1. Addition of zeolite to poultry litter paperboard significantly affected paperboard properties. It increased the thickness and apparent density and decreased the air resistance and strength properties of paperboards. By increasing the zeolite content, the capacity and rate of water absorption of paperboard were increased.
2. Zeolites are recommended as absorbent agents for poultry litter paperboard because one of the important factors in poultry litter efficiency is its water absorption properties. In this study, addition of zeolite to poultry paperboard caused up to a 44% increase in the water absorption capacity and a 52% increase in the water absorption rate (in other words, a 52% decrease in water absorption time).
3. This product can be a suitable alternative litter for the poultry industry, especially in some countries such as Iran that do not have alternative resources to satisfy the needs of the poultry industry.
4. It appears that zeolite could absorb water and humidity from poultry houses. Moreover, the absorption efficiency of zeolite could be enhanced by selecting zeolite with greater porosity than the zeolite used in this study.

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