# Treatment of wastewaters contaminated with zinc ions using natural zeolite as adsorbent in a fixed bed column

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## ABSTRACT

The potential of natural zeolite as a low-cost adsorbent was investigated for the removal of zinc from aqueous solution using a continuous fixed bed column. The zeolite tested was taken from the same source (Jabal Uniza in south Jordan) and subjected to crushing and sieving only, without any treatment. The two samples tested are UNZ1 (0.42–0.841 mm) and UNZ2 (0.21–0.42 mm). The Thomas model analysis of the measured breakthrough curves revealed that the adsorbent UNZ2 has a higher value of adsorption capacity to zinc ions (50.75 mg/g) than UNZ1 (33.68 mg/g). The time to 50% breakthrough was determined by the Yoon and Nelson model. It has been found that the time needed to reach 50% breakthrough is 2,006 minutes and 3,171 minutes for UNZ1 and UNZ2, respectively. This indicated that UNZ2 provides better performance with larger service time. Both UNZ1 and UNZ2 agreed to a high degree with the Thomas and Yoon and Nelson models.

**Key words** | adsorption, breakthrough, capacity, column, zeolite, zinc

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## INTRODUCTION

A significant global environmental challenge is the discharge of enormous amounts of polluted wastewater containing heavy metals due to industrial activities. Heavy metals such as lead, cadmium, zinc, mercury, lithium, and copper, if present in water at certain concentrations, are considered to be a major concern due to their toxicity and carcinogenicity, which may cause human health problems (Lu & Chiu 2006; Khan *et al.* 2008; Mishra & Patel 2009). Heavy metal ions are categorized as significant pollutants to the environment since due to their stability and persistency they cannot either be degraded or destroyed (Lim *et al.* 2012).

Contamination of industrial wastewater effluents with zinc metal ions has become an environmental concern (Bose *et al.* 2002; Wilson & Pyatt 2007). Huge amounts of wastewaters with high zinc ion ($Zn^{2+}$) concentrations are discharged to the environment by many industries, such as metal plating, the manufacture of batteries, metal fabrication, mining and mineral processing industries (Raut *et al.* 2012). Moreover, some contamination resulting from the dissolution of zinc has been detected in water flowing through galvanized pipes and fittings. It is worthwhile to mention that zinc in trace amounts is a significant metal for the growth and health of humans, animals and plants. However, it becomes toxic if it exceeds certain levels and can cause the desiccation of muscles, imbalance of electrolytes, stomach ache, vertigo, and disharmony (Veli & Alyuz 2007). Also, it has been reported that increased amounts of zinc might cause depression, lethargy, neurological signs such as seizures and ataxia, and increased thirst (Kurniawan *et al.* 2006). According to the World Health Organization (WHO), drinking water containing zinc at levels above 5 mg/L is not acceptable (Mishra & Patel 2009; Caliskan *et al.* 2011). It is therefore important for the industries producing such wastewaters to develop methods for zinc removal from aqueous solutions and the reduction of its concentration to acceptable levels before discharging it to the environment.

There are several classical physico-chemical methods that have been employed for the removal of zinc and

other heavy metal ions from contaminated wastewater effluents, such as chemical precipitation (Eccles 1999; Wang *et al.* 2004; Aziz *et al.* 2008), membrane filtration (Juang & Shiau 2000; Blöcher *et al.* 2003; Saffaj *et al.* 2004), ion exchange (Blöcher *et al.* 2003), reverse osmosis (Abu Qdaisa & Moussab 2004), nanofiltration (Lv *et al.* 2008; Khedr 2008), ultrafiltration (Trivunac & Stevanovic 2006; Barakat 2008), electrodialysis (Chen 2004; Jakobsen *et al.* 2004), photocatalysis (Yoona *et al.* 2009), solvent extraction (Simonin *et al.* 2003), coagulation–flocculation (Amuda *et al.* 2006), flotation (Żak 2012), and ion exchange (Muzenda *et al.* 2011). However, these methods have different disadvantages such as high operational cost, low removal efficiency, incomplete metal removal, high reagent or energy requirements, membrane fouling and generation of toxic sludge or other heavy metal-containing waste products (Barakat 2011). The search for new methods involving the removal of zinc metals from wastewaters with low costs, high removal efficiency, minimum sludge generation, and easier sludge disposal has attracted attention to adsorption.

Recently, adsorption has become one of the attractive treatment techniques for wastewater laden with zinc ions. Basically, adsorption is a mass transfer process by which zinc ions are transferred from the liquid phase to the surface of the adsorbent, and become bound by physical and/or chemical interactions. Various low-cost adsorbents derived from agricultural waste, industrial by-products, natural material, or modified biopolymers, have been recently developed and applied for treatment of zinc contaminated wastewater. There are many published research studies aimed at the development of adsorbents for removal of zinc ($Zn^{2+}$) ions from contaminated wastewater.

Natural zeolites are promising and efficient adsorbents for the removal of zinc ions from wastewater due to their physical and chemical properties (Dimirkou 2007). They are characterized by their widespread grids of channels and large contact area. Their chemical structure is characterized by a three-dimensional crystalline structure of tetrahedral silica or alumina anions of strong bonds with the high ability to act as substrates for adsorbing cations (Li *et al.* 2008).

This work investigates the utilization of a low-cost natural zeolite adsorbent, which is available in enormous reserves and does not require any treatment except for size reduction and sieving. The study examines its potential as an adsorbent for removal of zinc ions using fixed bed columns.

## EXPERIMENTAL

The adsorbent zeolite was obtained from the Jabal Uniza volcano cones located in southern Jordan. The dominating zeolites in Uniza zeolitic tuff are phillipsite as major (phillipsitic zeolitic tuff) and chabazite as minor minerals (Al Dwairi 2007; Al Dwairi *et al.* 2014). The physical and chemical characteristics of the adsorbent are published elsewhere (Al Dwairi & Gougazeh 2010). Uniza phillipsitic tuff samples were crushed using a jaw crusher with an aperture of 5 cm and then sieved into sizes 0.42–0.841 mm for UNZ1 adsorbent and 0.21–0.42 mm for UNZ2 adsorbent. The adsorbent is characterized by a high content of zeolitic minerals reaching about 85% (Al Dwairi 2007; Al Dwairi & Gougazeh 2010). The mineral content of the adsorbent used in these experiments was analyzed using X-ray diffraction (XRD). Figure 1 represents the XRD pattern of the phillipsite zeolitic tuff from the study area. The XRD analysis indicated that the zeolite used contains the minerals phillipsite, diopside, smectite, hematite, and chabazite.

Synthetic zinc heavy metal stock solution at a concentration of 1,000 mg/L was prepared by dissolving zinc chloride analytical grade (Merck p.a.) salt in double deionized water. The solution was then diluted to the required initial concentration of 20 mg/L.

An adsorption column apparatus was constructed to perform fixed bed column studies for the adsorption of zinc ions into UNZ1 or UNZ2 zeolite samples (Figure 2). The column was selected from glass material with the dimensions of 1 cm² cross-sectional area (i.e., 1.1 cm internal diameter) and a length of 40 cm. The granulated zeolite (UNZ1 or UNZ2) was packed in two columns. A bed height of 20 cm was fixed in all experiments. The mass of the adsorbent was constant in all experiments at 20 g and used in all tests. The solution was introduced into the column at a constant flow rate of 6.7 mL/min by gravity and adjusted using a valve and flowmeter fixed at the entrance to the column. The adsorption study was performed at room temperature (22 °C) and an initial pH of
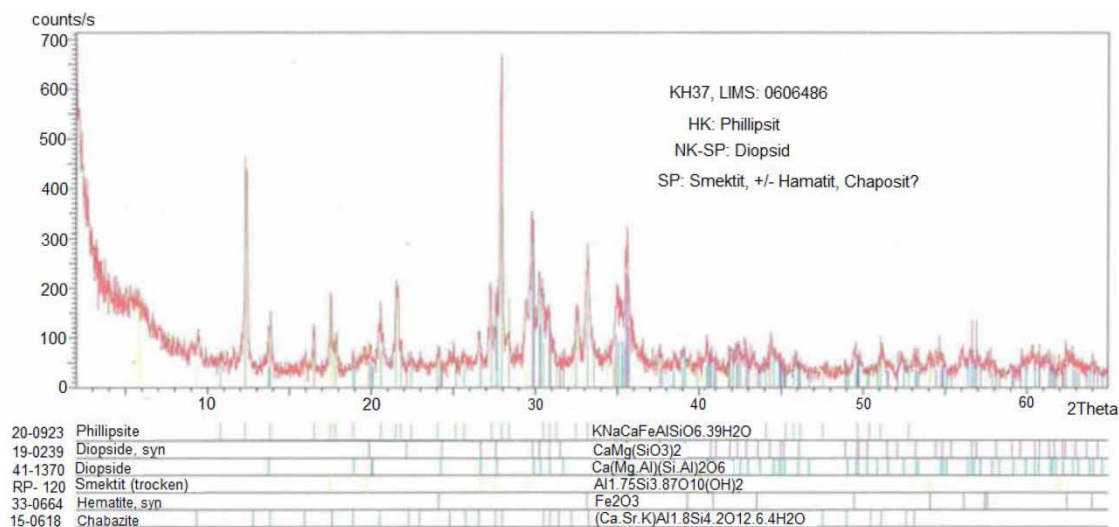
**Figure 1** │ The XRD pattern of the adsorbent phillipsitic zeolitic tuff from the study area (Al Dwairi & Gougazeh 2010).
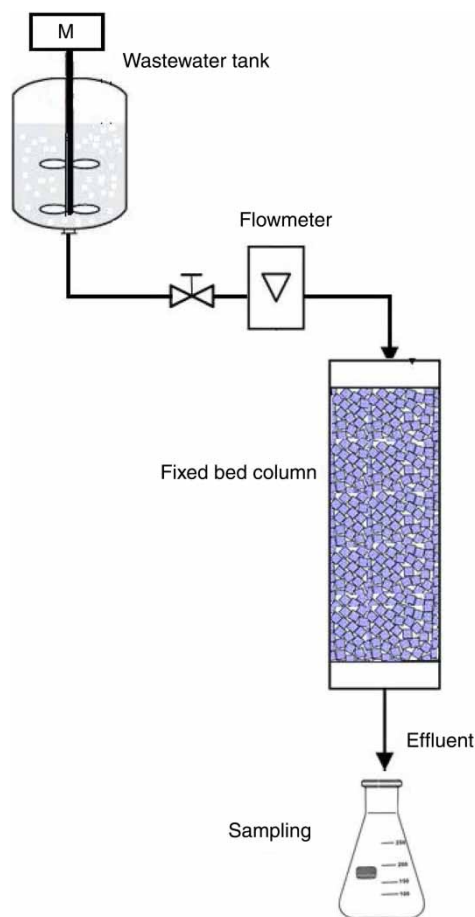


**Figure 2** │ Experimental fixed bed column used to perform fixed bed column studies for the adsorption of zinc ions into UNZ1 or UNZ2 zeolite samples.

5.47. The effluent samples were collected at specified intervals and analyzed for the residual ion concentration using an atomic adsorption spectrophotometer. Column studies were terminated when the column reached exhaustion. The experiments were conducted under constant conditions and the only variables to be studied were the adsorbent material (UNZ1 or UNZ2).

## RESULTS AND DISCUSSION

Experiments were conducted to investigate the column performance for the adsorption of the zinc ions using the two natural zeolite adsorbents, which varied only in the size of particles (UNZ1 and UNZ2). The column performance was studied by measuring breakthrough curves under identical conditions (initial pH 5.37; initial concentration 20 mg/L (ppm); flow rate 6.7 mL/min; mass of adsorbent 20 g; bed height 20 cm). The measured experimental breakthrough curves for the adsorption of zinc ions on UNZ1 and UNZ2 are presented in Figure 3, where the ratio of the effluent concentration ($C_e$) to the feed concentration ($C_0$) is plotted against time.

It is noticeable that the column performance for the adsorption of zinc ions on UNZ2 is more efficient than using the adsorbent UNZ1. It can be observed that the
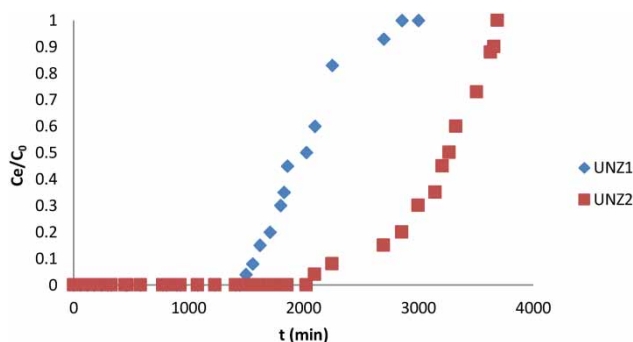
**Figure 3** | The measured breakthrough curves for the fixed bed adsorption of zinc ions on the zeolites UNZ1 and UNZ2.

breakthrough occurred earlier in the case of UNZ1. However the slopes of the breakthrough curves are almost identical for both adsorbents (UNZ1 and UNZ2). The enhanced adsorption and the improved column performance in the case of the zeolite UNZ2 can be attributed to the influence of grain size. The adsorbent UNZ2 has a grain size of 0.21–0.42 mm while the adsorbent UNZ1 has a grain size of 0.42–0.841 mm. Obviously, increasing the size of adsorbent particles reduces bed capabilities and thus reduces breakthrough time. The diffusion path is shorter for smaller grains, and therefore the adsorbate will more easily be adsorbed to the active sites of the zeolite particles. Moreover, smaller particles have a larger total exposed surface area and thus more active sites. Furthermore, the particle size has an important influence on the flow through the column. The smaller size particles lead to greater hydraulic resistance. This significantly influences the residence time of the solute in the column, which can be longer in the case of smaller particles. Therefore, there is a higher probability for adsorption equilibrium to be reached in the case of the smaller size particles, whereas in the case of larger size particles the solution is more likely to leave the column before equilibrium is reached.

## Mathematical modelling – Thomas model

The design of an adsorption packed column requires the determination of column parameters such as adsorption capacity and the kinetic parameters. The Thomas model can be implemented to analyze the breakthrough curves, illustrated in Figure 3, to determine the adsorption capacity

for each adsorbent. The Thomas model is also referred to as the bed-depth-service-time model. The mathematical representation of the Thomas model in its linearized form has the following form (Baek *et al.* 2007; Sivakumar & Palanisamy 2009):

$$ln\left(\frac{C_0}{C_e} - 1\right) = \frac{M\,q_0\,K_T}{Q} - \frac{C_0 K_T}{Q}\,V \tag{1}$$

where the kinetic parameters $K_T$ and $q_o$ are the Thomas rate constant (mL/min/mg) and the maximum adsorption capacity (mg/g), respectively. $V$ is the throughput volume (mL); $M$ is the total mass of the adsorbent (g), $C_e$ and $C_O$ are the effluent and inlet solute concentrations (mg/L), respectively; $Q$ is the volumetric flow rate (mL/min).

It is worthwhile mentioning that the Thomas model uses the familiar Langmuir isotherm. The mathematical expression described by Equation (1) is the modified form of the Thomas model, which is commonly used to fit the fixed bed breakthrough adsorption experimental data. This modified model assumes a rectangular (irreversible) isotherm when solving the differential mass balance equation for a fixed bed column, and is mathematically equivalent to the Bohart-Adams model (Chu 2010).

The kinetic coefficient, $K_T$, and the adsorption capacity of the bed, $q_o$, can be calculated by the plot of the measured breakthrough curves according to Equation (1). Thus, a plot of $ln\,[(C_o/C_e)-1]$ against $V$ at a given flow rate should give a straight line if the measurements follow the Thomas model (see Figure 4). The slope and intercept can be used to evaluate the kinetic parameters $K_T$ and $q_o$ (Table 1). Obviously, the measured breakthrough curves obey the Thomas model with a correlation coefficient range of $R^2 = 0.94$ for both UNZ1 and UNZ2.

The calculated Thomas model kinetic parameters in Table 1 reveal that the adsorbent UNZ2 has a higher value of adsorption capacity to zinc ions (50.75 mg/g) than UNZ1 (33.68 mg/g). In general, the zeolite used has a high capacity and can be used for long term operations for wastewater treatment by implementing fixed bed technology. The high adsorption capacity of the tested zeolites is attributed to their porous structure. Zeolites have a cage-like structure with open channels. On the other hand, zeolite has a high potential to exchange its alkaline cations with zinc ions.
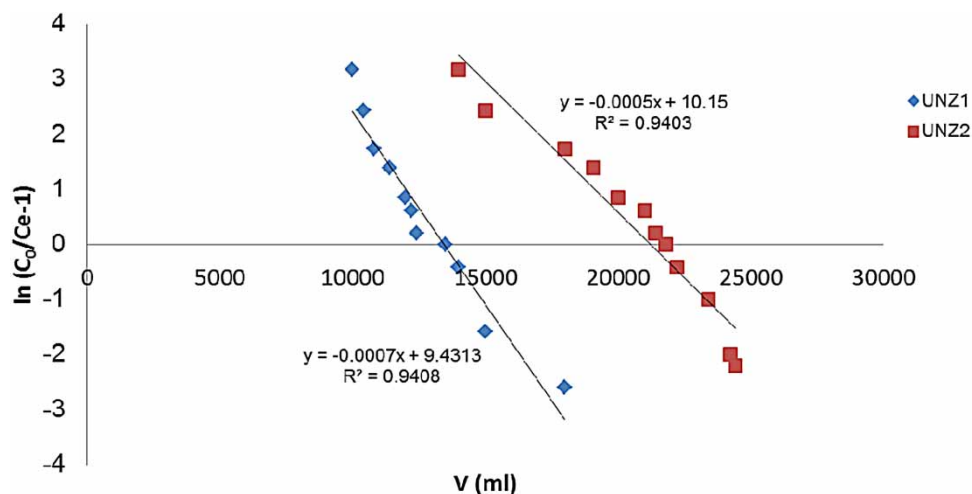
**Figure 4** | Plot of the measured breakthrough curves according to the Thomas model.

**Table 1** | Thomas model kinetic parameters for the fixed bed adsorption of zinc on UNZ1 and UNZ2 adsorbents

| Adsorbent | Slope | Intercept | $R^2$ | $K_T$ (mL/min/mg) | $q_o$ (mg/g) |
|---|---|---|---|---|---|
| UNZ1 | 0.0007 | 9.4313 | 0.9408 | 0.0938 | 33.68321 |
| UNZ2 | 0.0005 | 10.15 | 0.9403 | 0.067 | 50.75 |

The measured breakthrough curves (Figure 3) are compared with the calculated values estimated from the Thomas model (Equation (1)) using the kinetic parameters in Table 1 for the UNZ1 and UNZ2 zeolites. The theoretical curves calculated according to the Thomas model are shown in Figure 5. It can be seen that the theoretical curve calculated by the Thomas model is in good agreement with the measured experimental curves.
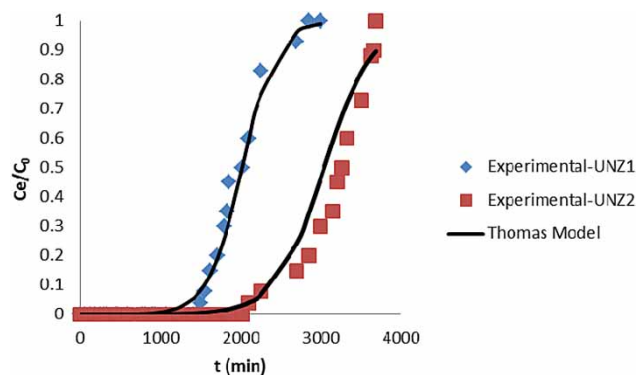


**Figure 5** | Comparison of experimental and calculated curves from the Thomas model for the adsorption of zinc using UNZ1 and UNZ2 zeolites.

The Thomas model fits the experimental data for the adsorption of zinc ions on UNZ1 and UNZ2 zeolites to a high degree, which reveals that the adsorption mechanism follows the second-order reversible reaction kinetics (Thomas 1944) and the adsorption behavior is controlled by both the chemical adsorption with an ion exchange process and electrostatic adsorption. The kinetic parameters calculated from the Thomas model can be implemented for the successful design of fixed bed wastewater treatment processes.

## Mathematical modeling – Yoon and Nelson model

The breakthrough curves in Figure 3 were analyzed using the Yoon and Nelson kinetic model. The linearized form of the Yoon and Nelson model is given by the following mathematical formula (Tsai *et al.* 1999):

$$ln\left(\frac{C_e}{C_0 - C_e}\right) = K_{YN}t - \tau.K_{YN} \qquad (2)$$

where $C_e$ and $C_o$ are the effluent and inlet zinc ions concentration (mg/L); $K_{YN}$ is the Yoon and Nelson rate constant (min$^{-1}$); $\tau$ is the time required for 50% adsorbate breakthrough (min) and $t$ is the bed service time (min). The plot of the experimental breakthrough curve (Figure 3) according to the linearized Yoon and Nelson model (Equation (2)) is displayed in Figure 6.
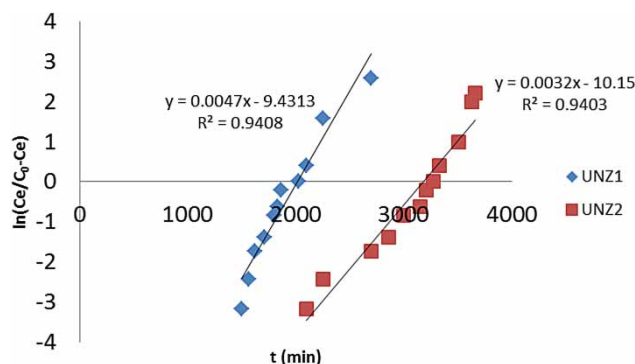
**Figure 6** | Plot of the measured breakthrough curves according to the Yoon and Nelson model.
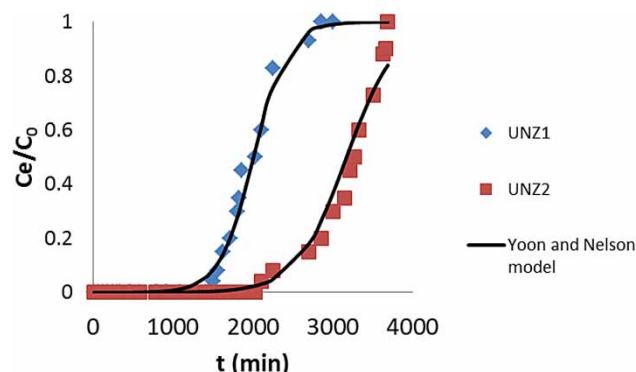


**Figure 7** | Comparison of experimental and calculated curves from the Yoon and Nelson model for the adsorption of zinc using UNZ1 and UNZ2 zeolites.

Clearly, the experimental breakthrough curves follow the Yoon and Nelson model with a correlation coefficient ($R^2 = 0.94$). The evaluated Yoon and Nelson model kinetic parameters $K_{YN}$ and $\tau$ and the regression coefficient $R^2$ are given in Table 2.

An important kinetic design parameter is the time to 50% breakthrough ($\tau$) determined by the Yoon and Nelson model. It gives an indication about the performance of the adsorbent to adsorb a certain adsorbate. By examining Table 2, it can be concluded that the time needed to reach 50% breakthrough is 2,006 minutes and 3,171 minutes for UNZ1 and UNZ2, respectively. This indicates that UNZ2 provides a better performance with longer service time.

Figure 7 shows the experimental breakthrough curves compared with the calculated values estimated from the Yoon and Nelson model. It can be seen that the theoretical curve calculated by the Yoon and Nelson model is in good agreement with the measured experimental curves. Also, it is clear that the Yoon and Nelson model fits the experimental data for the adsorption of zinc ions on UNZ1 and UNZ2 zeolites to a higher degree than the Thomas model.

## CONCLUSIONS

This work evaluates a Jordanian natural zeolite to be implemented directly after crushing and sieving as an adsorbent for treating wastewater contaminated with zinc ions. The obtained adsorption parameters indicated that an industrial scale continuous adsorption column process can be implemented successfully to treat enormous flow rates of wastewater streams due to the large breakthrough time and the adequate adsorption capacity of the tested natural zeolite. The size of the grains was found to be a crucial parameter in enhancing the service time and the maximum adsorption capacity. It is recommended to conduct further studies to understand the other operating parameters such as pH, flow rate, and bed height.

**Table 2** | Yoon and Nelson model kinetic parameters for the fixed bed adsorption of zinc on UNZ1 and UNZ2 adsorbents

| Adsorbent | Slope | Intercept | $R^2$ | $K_{YN}$ | $\tau$ (min) time to 50% breakthrough |
|-----------|--------|-----------|--------|----------|----------------------------------------|
| UNZ1 | 0.0047 | 9.4313 | 0.9408 | 0.0047 | 2,006.659574 |
| UNZ2 | 0.0032 | 10.15 | 0.9403 | 0.0032 | 3,171.875 |

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