Jordan Journal of Civil Engineering, Volume **3**, No. **3**, **2009**

The Use of Expendable Local Zeolite Deposits for NH_4 Removal in Municipal Wastewater

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ABSTRACT

Zeolitic tuff from Al-Tafila area (southern Jordan) has been investigated and tested for its uptake of ammonium (NH_4^+) from treated domestic wastewater using pilot plant scale column system. The zeolitic volcanic tuff from Jabal Al-Ataita is mainly represented by vitric and vitric crystal tuff. In this zeolitic tuff deposits, a percentage of about (46-65%) of volcanic glass in the pyroclastic sequence has been replaced by zeolites. The main zeolite species identified in volcanic tuffs from Al-Ataita volcano is phillipsite. The removal experiments were carried out depending on size fraction and bed depth of the zeolitic tuff. The used wastewater was collected from the treated wastewater effluent from Al-Tafila wastewater treatment plant. Breakthrough curves were constructed to differentiate between the ammonium removal efficiency using different size cuts of zeolitic tuff. The ammonium ions were completely removed from (32 ppm NH_4^+) solution onto 40 g of zeolitic material in the first time of filtration. Natural zeolitic tuff of 0.55-0.710 mm size fraction showed the highest breakthrough point and exhaustion point. The results of the study suggests that the zeolitic tuff of Jabal Al-Ataita with a size fraction of (0.55-0.710 mm) can be used as a final stage (following the biological process) in wastewater treatment plants in order to assure compliance with environmental standards.

KEYWORDS: Zeolitic tuff, Phillipsite, Jabal Al-Ataita, Jordan, Wastewater, Ammonium, Ionic exchange.

INTRODUCTION

Zeolites are a group of hydrated aluminum-silicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium). Zeolites have a three-dimensional crystalline framework of tetrahedral silica or alumina anions strongly bonded at all corners and contain channels filled with water and exchangeable cations (Mumpton, 1978). The structure is suitable for ion exchange due to isomorphous replacement of Al^{3+} with Si^{4+} in the structure, giving rise to a deficiency of positive charge in the framework. Zeolites may be used as ionic or molecular filters due to their particular crystal structure of a tectosilicate-type, characterized by pores with larger sizes than those of the ions (molecules) that pass through.

Earlier studies have shown that natural zeolites can be effective in removing ammonia from wastewater (Nguyen and Tanner, 1998). Ammonium removal by using zeolites as ion exchangeable material is also used in the aquaculture industry where water is recirculated (Dryden, 1984).

Zeolites were first discovered in Jordan by Dwairi (Dwairi, 1987) in the northeastern part. The Jordanian phillipsitic tuff from Aritayn area has a good efficiency in ammonium removal from wastewater, as well as

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Accepted for Publication on 15/7/2009.

Hungarian clinoptiololite, but phillipsite is more selective for ammonium ions (Dwairi, 1991). Attilli (1992) has evaluated the Jordanian phillipsitic tuff from Aritayn area for applications in water softing, removal of ammonium and toxic heavy metal ions in laboratory and pilot plant scale. Al-Rashdan (1994) has evaluated the effect of Jordanian phillipsitic zeolitic tuff from Jabal Aritayn on the removal of ammonium and phosphate from domestic wastewater. It was concluded that phillipsitic zeolitic tuff has shown acceptable efficiency in the removal of pollutants from the effluent.

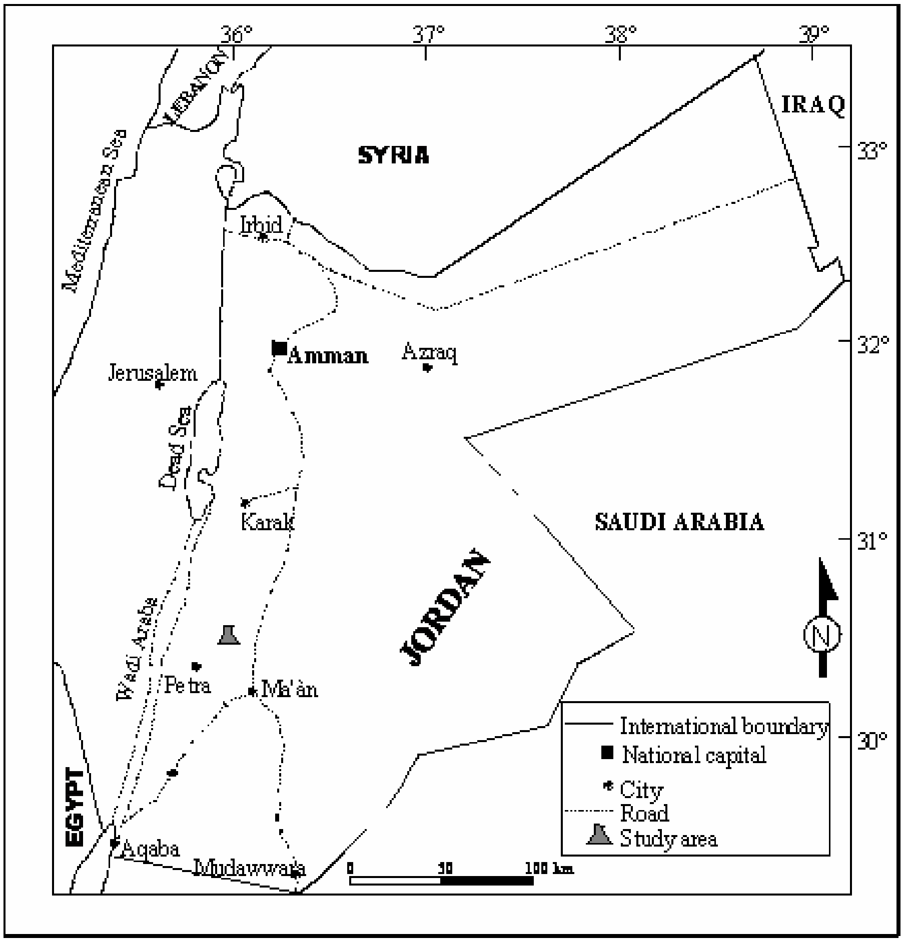

Figure (1): Location map of the study area.

Many types of rocks can contain usually small amounts of zeolites, but the main rock-type containing such minerals is the zeolitic volcanic tuff (Hay and Sheppard, 2001). The zeolitic tuff rocks from south Jordan associated with volcanic rocks belong to Neogene and Pleistocene (Bender, 1974). Al-Ataita volcano is one of the basalt volcanoes along the arched eastern rim of the graben (Fig. 1), and it belongs to Middle Pleistocene. The volcanic tuffs from the study area generally have a vitroclastic and vitric crystal texture and are zeolitized. They consist of 70-85 % of volcanic glass, 15-25% of crystals and lithic fragments in subordinate amounts (2-3%). The pyroclastic rocks belong to the Aritayn type and Hassan Type (Ghrir, 1998). The chemical composition of the zeolitic tuff from Jabal Al-Ataita has been studied and determined by Ghiri (1998), Table (1). Jabal Al-Ataita zeolitic tuff has been investigated and characterized by Al Dwairi (2007), who found that the dominating zeolitic tuff mineral is phillipsite with minor amounts of chabazite. Phillipsite is a hydrated potassium sodium calcium alumina-silicate member of the harmotome family and is one of the more useful natural zeolites. Past research has shown that the natural zeolite, phillipsite, is highly selective for ammonium over most other cations in an aqueous solution.

In this paper, the used techniques investigates the uptake rate of ammonium ions by the Jordanian phillipsite zeolite from Jabal Al-Ataita, south Jordan.

Table (1): Chemical composition of the bulk volcanic zeolitic tuff from Al-Ataita volcano (Ghrir, 1998).

Sample	SiO_2 [%]	Al_2O_3 [%]	TiO_2 [%]	Fe_2O_3 [%]	CaO [%]	MgO [%]	Na_2O [%]	K_2O [%]	LOI [%]
1	42.61	11.29	3.00	11.98	9.75	6.68	0.84	0.77	13.32
2	40.85	11.07	3.26	12.89	11.13	7.35	0.84	0.35	12.15
3	41.44	11.51	3.41	13.27	11.52	6.85	0.62	0.65	12.50

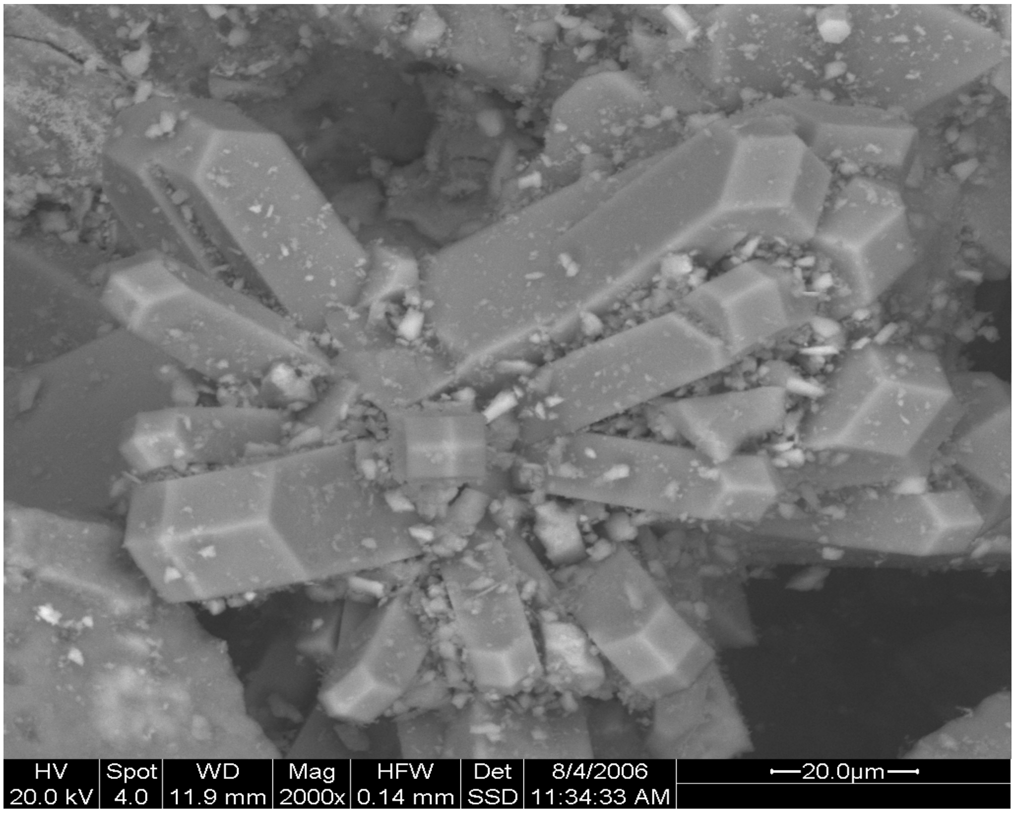

Figure (2): Scanning electron micrographs of zeolitic tuff samples from Jabal Al-Ataita showing radial growth of phillipsite crystals.

Table (2): Size fraction and bed depth for the used zeolitic tuff samples.

Column #	**Size fraction (mm)**	**Bed depth (cm)**	**Bed Volume (BV) (mm)**
AZ1	-1+0.850	10, 20, 30 and 40	10, 20, 30 and 40
AZ2	-0.850+0.550	10, 20, 30 and 40	10, 20, 30 and 40
AZ3	-0.550+0.355	10, 20, 30 and 40	10, 20, 30 and 40

Table (3): Chemical composition of the sieved zeolitic volcanic tuff from Al-Ataita volcano.

Sample	**SiO_2 [%]**	**Al_2O_3 [%]**	**TiO_2 [%]**	**Fe_2O_3 [%]**	**CaO [%]**	**MgO [%]**	**Na_2O [%]**	**K_2O [%]**	**LOI [%]**
AZ1	40.95	11.10	3.19	12.57	10.96	7.20	0.89	0.47	11.90
AZ2	41.69	11.49	3.30	12.90	11.60	7.10	0.63	0.55	12.40
AZ3	43.26	12.97	3.70	11.30	9.70	5.78	0.96	0.44	11.89

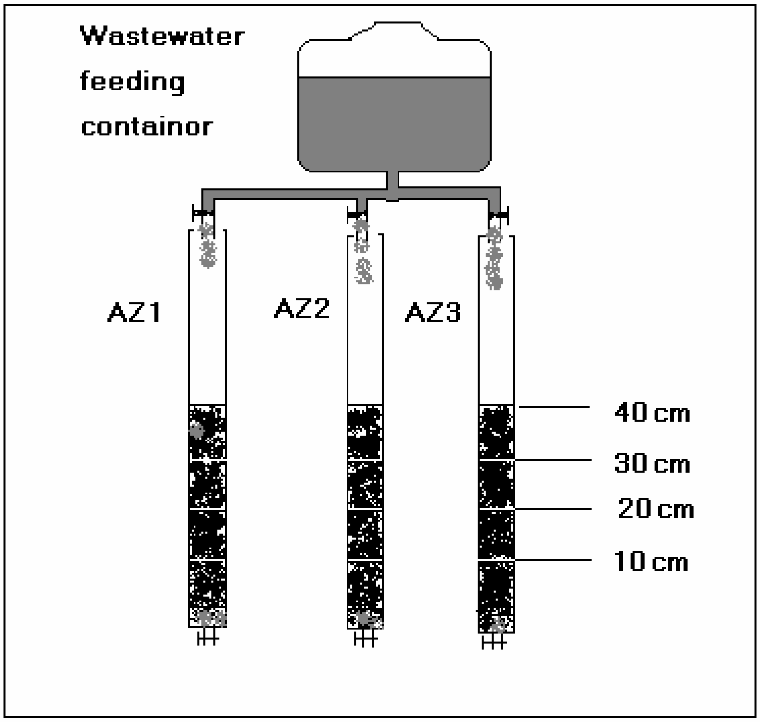

Figure (3): Bench scale plant method using different samples of Jordanian phillipsitic zeolitic tuff and different bed depths from Jabal Al-Ataita zeolitic tuff.

MATERIALS AND METHODS

MATERIALS

Twenty fresh representative zeolitic tuff channel samples were collected from Al-Ataita volcano. The processing stages involved in the zeolite preparation were as follows: crushing, wet size separation, washing with distilled water and drying at 105°C for 8 hours. Each sample was sieved into three size fractions to be used in removal experiments (Table 2). The chemical composition of the samples is listed in Table (3). Treated domestic wastewater of known ammonium concentration was collected from the effluent of Al-Tafila wastewater treatment plant (Table 4).

Table (4): Chemical characteristics of Al-Tafila wastewater treatment plant effluent wastewater.

	Concentration (ppm)
NH_4	32
TOC	59-51
Pb	2.1
Zn	1.7
Ni	0.06
Cd	0.005
Mn	0.08

PILOT COLIUMN

A three pilot-scale column was designed and fabricated for continuous adsorption of ammonia from domestic treated wastewater. An outline drawing of the columns is given in Figure (3). The used apparatus is made up of 100 cm of glass column with 1 cm^2 base area with 3 cm of rock wall used to support the zeolite bed and prevent the zeolite from being lost through the holes in the base plate. Approximately 10, 20,30 and 40cm of phillipsite zeolite (AZ1, AZ2 and AZ3) were loaded and gently packed into three columns, each column for each sample. The service step took place by feeding the effluent in down-flow direction. For each zeolitic tuff fraction size a pilot-scale column was placed. The experiments were carried out in two sets of experiments; set one examined the effect of particle size with bed depth, while set two was carried out to distinguish between the different bed depths for the best removal size fraction. The NH_4^+ concentration of the inlet (original) was 32 ppm. The effluent NH_4^+ solution was collected at the outflow of the columns at every bed volume until the zeolitic tuff was exhausted. The NH_4^+ concentrations were measured for each bed volume successively sampled. The experiments were realized at room temperature (20°C) and pH of 7.1.

RESULTS AND DISCUSSION

The results obtained from the pilot-scale experiments were represented using ideal breakthrough curves for NH_4^+ removal as presented in Figures (4, 5, 6, 7 and 8) and listed in Table (5).

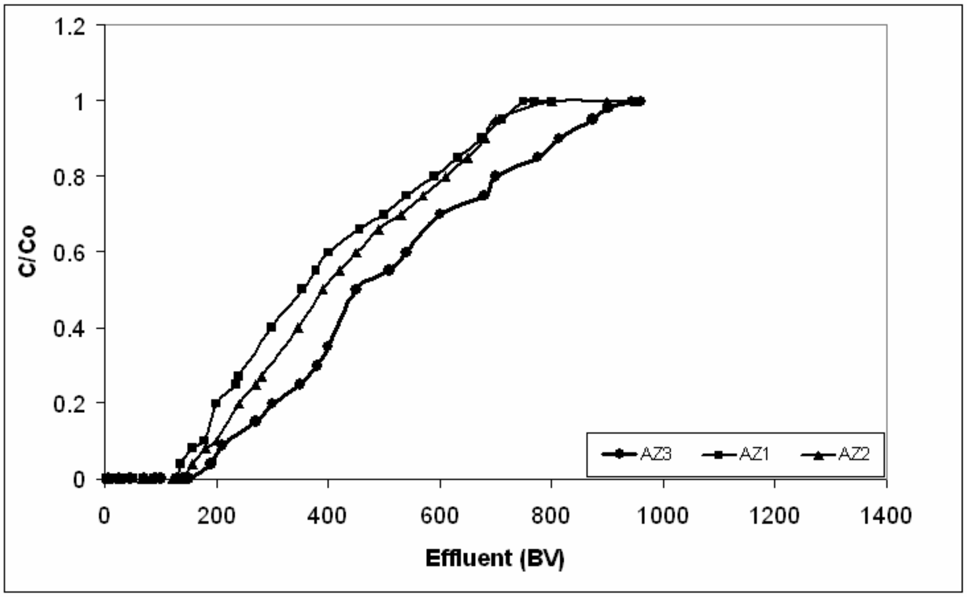

Figure (4): Ideal breakthrough curves for ammonium sorption using 10 cm of AZ1, AZ2 and AZ3 zeolitic tuff samples.

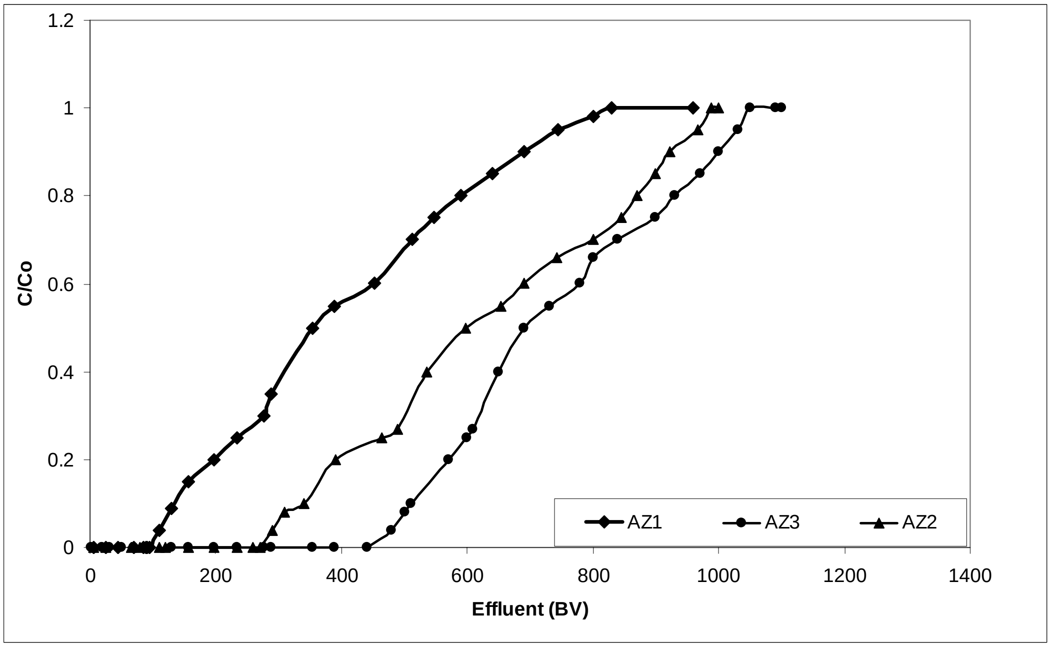

Figure (5): Ideal breakthrough curves for ammonium sorption using 20 cm of AZ1, AZ2 and AZ3 zeolitic tuff samples.

Table (5): Breakpoint, exhaustion point and total treated wastewater for different bed depths for AZ1, AZ2 and AZ3 zeolitic tuff samples from Al-Ataita volcano.

Sample	Bed Depth (cm)	Break Point (BV)	Exhaustion Point	Total Treated W.W. in Bed Volume (BV)	Total Treated W.W. in Liters (L)
AZ1	10	130	712	750	7.5
	20	111	800	830	16.600
	30	260	800	834	25.02
	40	300	1000	1032	41.28
AZ2	10	135	699	800	8.0
	20	290	967	989	19.78
	30	342	1030	1070	32.10
	40	360	999	1040	41.6
AZ3	10	156	901	943	9.43
	20	440	1030	1050	21.00
	30	580	1100	1150	34.50
	40	650	1190	1220	48.80

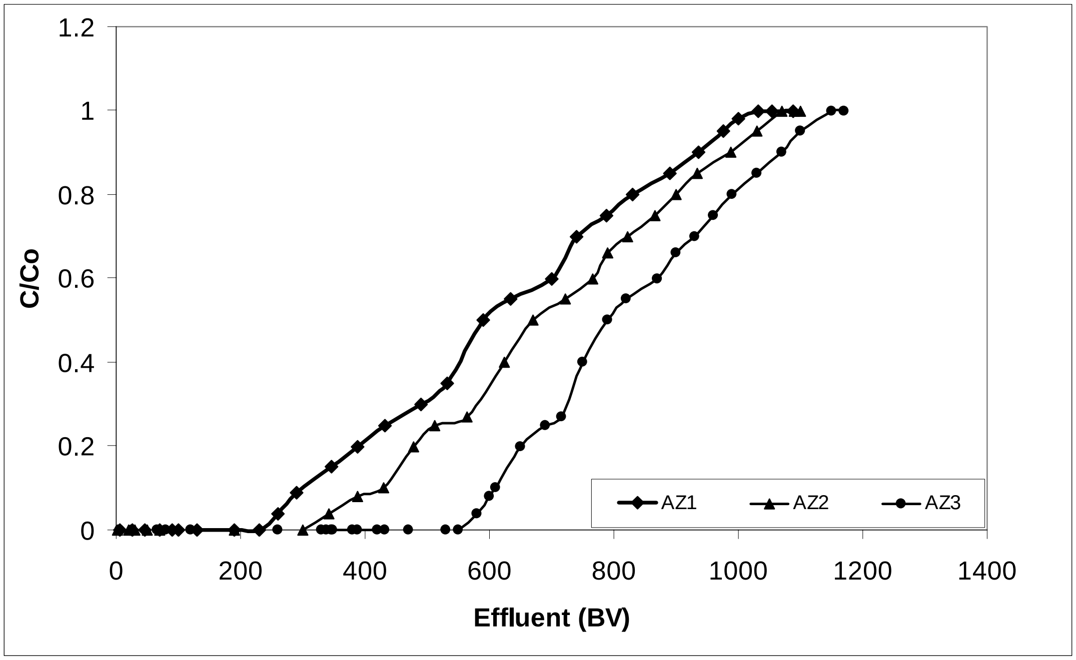

Figure (6): Ideal breakthrough curves for ammonium sorption using 30 cm of AZ1, AZ2 and AZ3 zeolitic tuff samples.

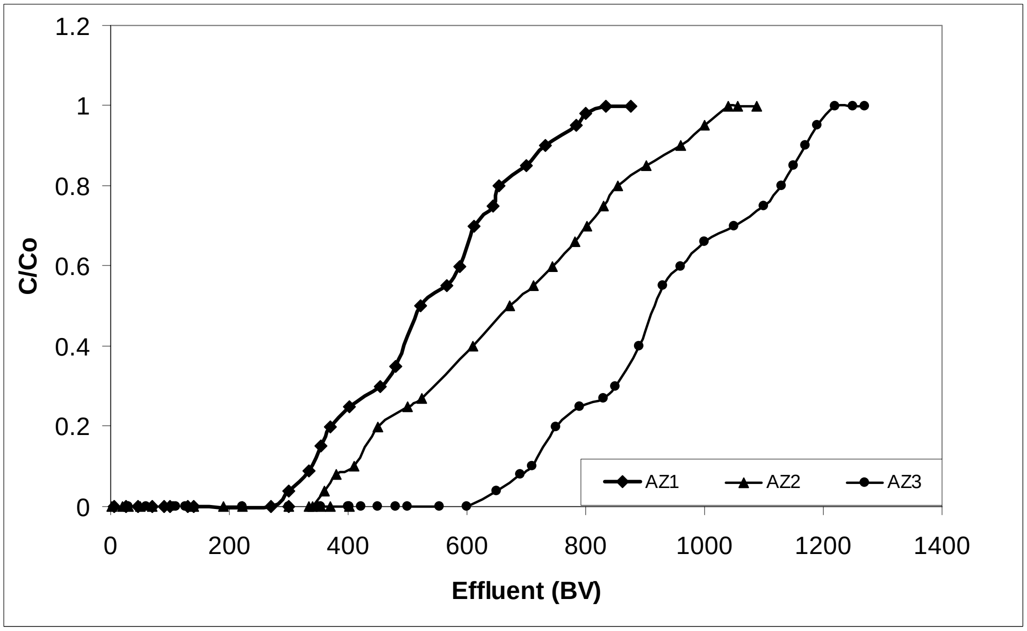

Figure (7): Ideal breakthrough curves for ammonium sorption using 40 cm of AZ1, AZ2 and AZ3 zeolitic tuff samples.

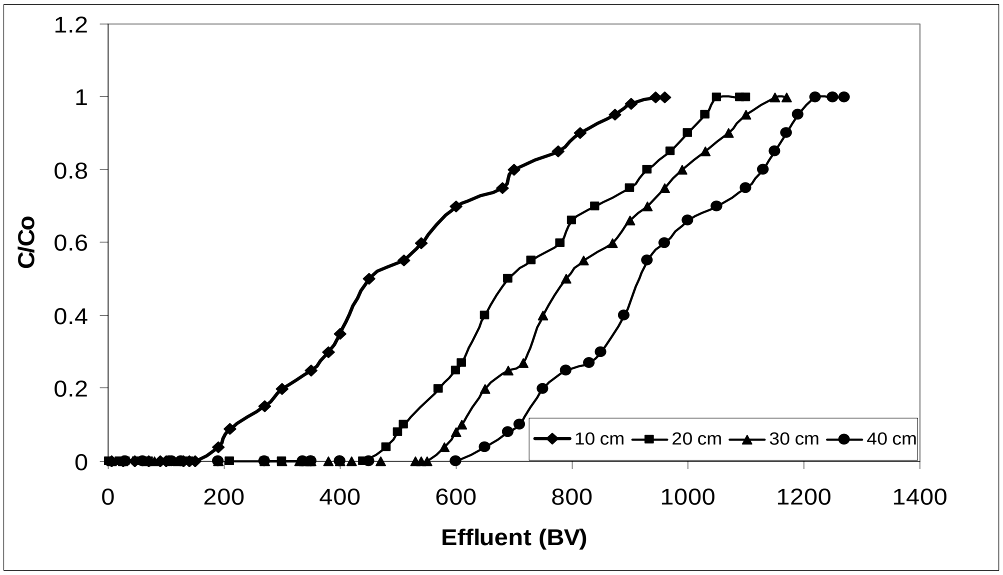

Figure (8): Ideal breakthrough curves for ammonium sorption using 10,20, 30 and 40 cm AZ3 zeolitic tuff sample.

The breakthrough curves for absorption experiments show three major stages during the absorption process of NH_4^+ ions:

(1) a complete adsorption of the NH_4^+ ions from the solution onto the zeolitic material during the first stage (C/Co = 0).

(2) The second stage when NH_4^+ ions began to appear in the collected treated samples (breakpoint) (C/Co > 0 and < 1).

(3) Exhaustion stage when the concentration of influent was equal to the concentration of effluent treated wastewater (exhaustion point) (C/Co = 1).

EFFECT OF PARTICLE SIZE AND BED DEPTH

The results listed in Table (5) show breakpoint, exhaustion point and total treated wastewater for different bed depths for AZ1, AZ2 and AZ3 zeolitic tuff samples from Al-Ataita volcano area. The results indicate that AZ3 zeolitic tuff with bed depth = 40 cm has a breakpoint of 650 (BV), an exhaustion point of 1190 (BV) and the highest amount of treated water (48.8 L) unless the sample was exhausted. Figures (4, 5, 6 and 7) show the breakthrough curves for ammonia removal by natural zeolite using three different particle size cuts AZ1 (-1+0.850), AZ2 (-0.850+0.550) and AZ3 (-0.550+0.355) and different bed depths. The results indicated that the use of AZ3 zeolitic tuff of different bed depths (10, 20, 30 and 40cm) showed the highest ammonium uptake.

The results for different bed depths using AZ3 particle size fraction are represented in Figure (8). The breakthrough curves indicate that the use of 40cm of AZ3 bed depth gives the best ammonia removal.

CONCLUSIONS

The highest NH_4^+ uptake was observed in the case of using 40 cm of AZ3, so AZ3 is considered the best size fraction which can be used as ion exchangeable bed, and this size fraction can be considered the highest zeolite percentage content. The NH_4^+ ionic exchange process on zeolitic volcanic tuffs from south Jordan can be used as a finishing stage (after the biological process) in wastewater treatment plants after sieve sizing. After the ionic exchange process has taken place, the zeolite samples in Z- NH_4^+ form (exhausted) can be regenerated and reused in the same process or can be used as fertilizer.

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