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Ammonium removal from wastewaters using natural New Zealand zeolites

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Abstract Ammoniacal nitrogen (ammonia and ammonium) in agricultural wastewaters can promote eutrophication of receiving waters and be potentially toxic to fish and other aquatic life. Zeolites, which are hydrated aluminum-silicate minerals, have an affinity for ammonium ions (NH_4^+) and are, therefore, potentially useful in removing this contaminant from wastewaters. The major objectives of this study were to evaluate the capacity of two natural New Zealand zeolites (clinoptilolite and mordenite) to remove NH_4^+ from a range of wastewaters under both batch and flow-through conditions. Effects of two zeolite particle size ranges (0.25–0.50 mm and 2.0–2.83 mm) on NH_4^+ removal performance were also investigated. Results obtained from the batch adsorption experiments indicated that both zeolites tested, regardless of their particle sizes, were equally effective (87–98%) at NH_4^+ removal from domestic wastewaters or synthetic solutions containing NH_4^+ concentrations of up to 150 g NH_4-N m^{-3}. However, mordenite showed more effective NH_4^+ removal than clinoptilolite for dairy and piggery wastewaters, and for synthetic solutions containing high NH_4^+ concentrations (350–750 g NH_4-N m^{-3}). At all equilibrium NH_4^+ concentrations tested (0.2–300 g NH_4-N m^{-3}), NH_4^+ removal by both mordenite and clinoptilolite was significantly ($P < 0.0001$) reduced by the presence of competing sodium (Na^+) cations in the synthetic solutions. The maximum amounts of NH_4^+ removed by coarse and fine clinoptilolite and coarse and fine mordenite, calculated by the Langmuir model, were 5.77 and 5.74, and 8.09 and 8.28 g NH_4-N kg^{-1}, respectively. In the slow flow-through experiment (0.47 mm min^{-1}), NH_4^+ breakthrough (>1.2 g NH_4-N m^{-3}) for both zeolite sources (regardless of their particle sizes) did not occur even after receiving 40 bed volumes (BV) of wastewaters containing 100 g NH_4-N m^{-3}. The NH_4^+ removal at this breakthrough was approximately 99 g NH_4-N m^{-3} of wastewater throughput, which equates up to 5.8–6.5 g NH_4-N kg^{-1} zeolite. In contrast, at a faster loading flow rate (15.9 mm min^{-1}), the breakthrough was almost immediate (1 BV) for coarse zeolites and after 22 BVs for fine zeolite. The NH_4^+ breakthrough capacity for fine mordenite was 2.0–4.4 g NH_4-N kg^{-1} zeolite. Fine zeolites were more effective than coarse zeolites in removing wastewater NH_4^+ (95% and 55% removal, respectively), even after receiving 64 BV of wastewater.

Keywords zeolite; clinoptilolite; mordenite; ammonium removal; wastewater; dairy effluent; piggery effluent; synthetic effluent; agricultural wastewaters

INTRODUCTION

Zeolites are crystalline hydrated alumino-silicates, which are known to have an affinity for ammonium (NH_4^+) and other cations (Pansini 1996). Overseas studies have established that zeolites have the potential to remove NH_4^+ from municipal, industrial, and aquacultural wastewaters (e.g., Liberti et al. 1979; Beler-Baykal et al. 1996; Booker et al. 1996; Pansini 1996). The capacity of zeolites to remove NH_4^+ from wastewaters has been found to vary, depending on the type of zeolite used (e.g., mordenite, clinoptilolite, erionite, chabazite, and phillipsite), zeolite particle size, and wastewater anion-cation composition (Koon & Kaufman 1975;

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Jorgensen et al. 1976; Klieve & Semmens 1980). This capacity is also governed by the extent of aluminium (Al^{3+}) substitution for silicon (Si^{4+}) in the zeolite framework (Barrer 1978; Bohn et al. 1979). Each Si^{4+} substitution by Al^{3+} generates a negative charge. The greater the substitution, the higher the negative charge, and hence the greater the number of cations (e.g., NH_4^+) required for balancing the negative charge.

Naturally occurring zeolites such as mordenite and clinoptilolite are found in both North and South Islands of New Zealand (Coombs 1959; Sameshima 1978). They are similar to overseas zeolites (Jorgensen et al. 1976; Czaran et al. 1988; Beler-Baykal et al. 1996; Curkovic et al. 1997) in terms of Si:Al and Si:(Al + Fe) ratios (ratios of 4.0:1–5.3:1; Coombs 1959; Sameshima 1978). On the basis of these chemical characteristics, the negative charge on the surface of the New Zealand mordenites and clinoptilolites and hence their NH_4^+ removal capacities are expected to be similar to those in overseas zeolites. However, the structural characteristics (e.g., porosity, density, and channel length) and the composition and exchangeability of Ca, Na, K, and Mg cations in zeolites, amongst other factors (e.g., zeolite particle size and zeolite concentration in the host rocks) are also known to influence zeolite capacity to remove NH_4^+ from wastewaters (Barrer 1978; Czaran et al. 1988; Booker et al. 1996; Curkovic et al. 1997). Clearly, the NH_4^+ removal capacities and performance of zeolites cannot be predicted by a single zeolite chemical-physical parameter. There is, therefore, a need to evaluate the capacity of different natural New Zealand zeolites to remove NH_4^+ from a range of wastewaters, particularly with increasing awareness of the potential impacts of ammoniacal N (ammonium and ammonia) in agricultural wastewater discharges on water quality in New Zealand (Smith et al. 1993).

In New Zealand, agricultural wastewaters such as those produced from daily washing of milking parlours and piggeries, are often treated in oxidation (or waste stabilisation) pond systems. However, ammoniacal N levels in pond effluent discharges are often excessive; for example, Hickey et al. (1989) found a median of 75 g m^{-3} for farm dairy ponds and Sukias & Tanner (1995) found medians for piggery pond discharges often in excess of 200 g m^{-3}. Thus, these pond effluents require substantial dilutions to reach an acceptable standard (0.22–0.77 g m^{-3}) for safe discharge to receiving streams (Davies-Colley 1996). There is also a need for further removal of ammoniacal N from agricultural pond discharges, after additional treatment in constructed wetlands (e.g., only 10–50% of NH_4^+ in pond wastewaters are removed; Sukias et al. 1996; Tanner & Kloosterman 1997).

The potential use of zeolites for removal of NH_4^+ from New Zealand agricultural wastewaters was recognised by Cooke et al. (1992). If natural New Zealand zeolites have a strong capacity to remove NH_4^+ from pond discharges, they may be used at the end of a two-pond system or within an oxidation pond–constructed wetland sequence as a filtering bed. Clogging of zeolite pores with suspended solids (SS) may not be a major problem if these wastewaters have been treated in an oxidation pond–wetland sequence, since wetlands commonly remove 70% of SS in wastewaters (Tanner & Kloosterman 1997). Even in farms where land application is a preferred alternative to a two-pond system, zeolites may play a useful role as an absorbing medium for NH_4^+. In these farms, wastewaters may be initially passed through zeolite beds before being applied to soils (particularly soils with a low nitrate retention capacity) to minimise the risk of groundwater nitrate pollution (by absorption of applied ammoniacal N in zeolites, thus minimising its nitrification to nitrate for leaching) and to reduce the agricultural area required for land application of wastewaters. Zeolite which was previously used to treat wastewaters, may then be strategically applied to farm areas where soil amendment or soil fertility enhancement is required.

The main objectives of this study were, therefore, to provide information on the NH_4^+ removal capacity of two different New Zealand zeolites and the influence of zeolite particle size, wastewater type and NH_4^+ content, and wastewater loading flow rate on this removal capacity.

MATERIALS AND METHODS

Materials

Two New Zealand zeolites (clinoptilolite and mordenite) from two different sources were sieved and bulked into 0.25–0.5 mm and 2–2.83 mm particle size ranges (termed fine and coarse, respectively; Table 1), and evaluated for their ability to remove NH_4^+.

Both batch (shaking a fixed quantity of zeolites with a fixed volume of a test solution) and flow-through (leaching column) experiments were used in this evaluation. Duplicate subsamples of the

studied zeolites were also taken for physical-chemical analyses.

Zeolite physical and chemical analyses

Duplicate samples of each zeolite were analysed for moisture content after drying at 105°C for 24 hours (Allen 1989), water saturation capacity (Allen 1989), loss on ignition (550°C for 5 hours, Allen 1989), pH in water or 1 N KCl suspension (zeolite:suspension ratio of 1:5; Blakemore et al. 1981), cation exchange capacity (Chapman 1965), surface area (Carter et al. 1965), and bulk density, particle density, and porosity using the methods described by Schoeman (1986).

Silicate (Si) in zeolites was determined colorimetrically using the blue silicomolybdous acid complex method of Hallmark et al. (1982). Aluminium (Al), total Kjeldahl nitrogen (N), potassium (K), magnesium (Mg), sodium (Na), iron (Fe), zinc (Zn), calcium (Ca), and total phosphorus (P) in zeolites were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) method (Soltanpour et al. 1982) after these zeolites had been digested with nitric-perchloric acid mixture.

Ammonium removal studies

Both batch adsorption and flow-through studies were conducted at ambient temperature in an air-conditioned room (21 ± 1°C).

Batch adsorption study

Triplicate zeolite samples (2 g per sample) were shaken for 17 hours on an end-over-end shaker (150 rpm) with 20 ml of:

(i) Ammonium chloride (NH_4Cl) solutions containing a range of NH_4^+ concentrations (15, 150, 350, and 750 g NH_4-N m^{-3}; ammoniacal concentration measured as nitrogen in ammonium form (NH_4-N).

(ii) Four different isonormal ammonium chloride-sodium chloride (NH_4Cl-NaCl) solutions (total 0.1 *M*). The NH_4Cl and NaCl concentrations in these isonormal solutions were 0.001, 0.01, 0.025, and 0.05 *M* (i.e., containing 14, 140, 350, and 700 g NH_4-N m^{-3}) and 0.099, 0.09, 0.075,

Table 1 Characteristics of the zeolites studied.

		Clinoptilolite		Mordenite	
Parameter	Unit	Coarse (2–2.83 mm)	Fine (0.25–0.50 mm)	Coarse (2–2.83 mm)	Fine (0.25–0.50 mm)
pH (H_2O)		5.4	5.4	8.5	8.2
pH (KCl)		3.5	3.5	7.2	7.3
Particle size		–	–	–	–
0.25–0.354 mm	%	–	67	–	67
0.354–0.50 mm	%	–	33	–	33
2.0–2.38 mm	%	71	–	71	–
2.38–2.83 mm	%	29	–	29	–
Surface area	$m^2\ g^{-1}$	40	40	25.5	30.1
Bulk density	$g\ cm^{-3}$	0.66	0.59	1.0	1.1
Particle density	$g\ cm^{-3}$	1.8	2.2	2.1	2.4
Porosity	%	61.9	72.9	51.7	56.1
Moisture content	%	7.6	6.6	4.6	4.3
Loss on ignition	%	7.6	6.6	6.6	5.6
Water holding capacity	%	102	95	46.7	54.7
Cation exchange capacity	me.%	100	105	110	116
Calcium (Ca)	%	0.72	0.73	4.2	4.3
Magnesium (Mg)	%	0.15	0.15	0.27	0.27
Potassium (K)	%	0.75	0.74	0.16	0.17
Sodium (Na)	%	0.47	0.41	1.26	1.25
Iron (Fe)	%	0.83	0.81	1.63	1.69
Zinc (Zn)	$mg\ kg^{-1}$	0.004	0.004	0.006	0.006
Aluminum (Al)	%	2.4	2.4	4.2	4.2
Silica (Si)	%	13.7	13.7	24.5	25.6
Nitrogen (N)	%	0.05	0.04	0.05	0.05
Phosphorus (P)	%	0.005	0.005	0.008	0.008

and 0.05 *M*, respectively. These solutions were used in order to maintain a constant ionic strength in the zeolite:solution mixture (Weber et al. 1983; Bernal & Lopez-Real 1993).

(iii) Four different wastewaters with three levels of NH_4^+ concentrations (Table 2). Wastewaters from the second pond of waste stabilisation systems treating domestic sewage, piggery, and farm dairy wastewaters were collected one day prior to the initiation of the study and stored at 4°C. They were diluted with distilled water to three levels of NH_4^+ concentrations ranging between 5 and 400 g NH_4-N m^{-3} (Table 2). These wastewaters were used to investigate the influence of wastewater composition and NH_4^+ concentration on the NH_4^+ removal capacity of zeolites. The synthetic effluent solution (Table 3) was prepared using the same chemical composition as that used by Klieve & Semmens (1980). It contained no organics or suspended solids.

A 17-hour equilibration period was chosen since NH_4^+ removal by the studied zeolites was found to be rapid (2–3 hours) but did not reach a steady state until after 16–17 hours (M. L. Nguyen unpubl. data). After 17-hour equilibration, zeolite-solution mixtures were centrifuged at 1360 RCF (relative centrifugal force) (i.e., 3000 rpm) for 5 minutes, and the supernatant solutions were analysed for NH_4^+. Amounts of NH_4^+ adsorbed by zeolites were determined by the difference between amounts of NH_4^+ initially added to the zeolites and those remaining in the supernatant solutions.

Flow-through study

To provide information on NH_4^+ adsorption under more realistic conditions, a flow-through study was conducted, using zeolite-packed polyvinyl chloride columns (2.5 cm internal diameter and 60 cm long) with a perforated (1.5 mm internal diameter) cap attached to the end of each column for drainage (Table 4). Clinoptilolite-packed columns received two different wastewater treatments (synthetic and dairy), and mordenite-packed columns received three different wastewater treatments (synthetic, dairy, and piggery; Table 5). Each of these treatments was duplicated. Dairy and piggery wastewaters collected from the second pond of two-pond waste stabilisation systems were stored at 4°C until the initiation of the flow-through experiment (one day after wastewater collection).

Wastewater treatments (thereafter referred to as feed solutions or influents) were continuously

Table 2 Some chemical properties of wastewaters and synthetic solutions mused in the batch study. See text for abbreviations. * not measured.

Wastewater		NH_4-N (g m^{-3})	PO_4-P (g m^{-3})	pH	BOD (g m^{-3})	COD (g m^{-3})	SS (g m^{-3})	Conductivity (mS cm^{-1})	Ca^{2+} (g m^{-3})	Mg^{2+} (g m^{-3})	Na^+ (g m^{-3})	K^+ (g m^{-3})	Cl^- (g m^{-3})	SO_4^{2-} (g m^{-3})
Piggery	High	400	34.2	7.87	180	560	185	280	46	30	73	278	160	23
	Medium	320	28.2	7.71	*	*	*	*	*	*	*	*	*	*
	Low	75	9.3	7.70	*	*	*	*	*	*	*	*	*	*
Dairy	High	180	24.7	7.41	100	290	165	100	38	11	33	215	136	18
	Medium	105	21.7	7.36	*	*	*	*	*	*	*	*	*	*
	Low	53	11.8	7.32	*	*	*	*	*	*	*	*	*	*
Domestic	High	29	5.6	7.80	40	198	61	73	20	9	25	107	58	11
	Medium	11	1.9	7.90	*	*	*	*	*	*	*	*	*	*
	Low	5.2	1.1	7.62	*	*	*	*	*	*	*	*	*	*
Synthetic		14	8.7	7.50	*	91	*	*	29	7	57	21	*	64

applied to the tops of the columns at 0.47 and 15.9 mm min^{-1} (i.e., 0.056 and 3.12 zeolite bed volumes (BV) per hour, respectively) using peristaltic pumps. Samples of leachate (thereafter referred to as effluent) were then collected from beneath each PVC column every 1–2 BV for NH_4^+ analysis.

The slow loading flow rate was carried out to resemble that likely in constructed wetlands, whereas the fast flow rate was designed to assess the capacity of the zeolite with the highest capacity to remove NH_4^+ (as shown from the batch and slow flow-through experiments) in situations where wastewaters would pass more rapidly through a zeolite bed (e.g., pulsed loadings of wastewaters from stock yards).

In the fast flow rate experiment, feed solutions were added until NH_4^+ concentration in the leachate (effluent NH_4^+ concentration) became similar to or approximately 50–90% of that in the feed solution, indicating that adsorption sites on zeolites were approaching saturation with NH_4^+. Since such saturation may take several weeks to achieve in the slow flow-through study, application of feed solutions was stopped when effluent NH_4^+ concentration was approximately 1.2 g NH_4-N m^{-3}. In an agricultural setting where wastewater is treated with zeolites before being discharged into receiving water, NH_4^+ breakthrough of 1.2 g NH_4-N m^{-3} is subsequently diluted with receiving waters, and therefore unlikely to elevate NH_4^+ concentration in receiving water to levels that exceed critical NH_4^+ thresholds (0.2–0.75 g m^{-3}; Davies-Colley 1996). Thus the selected level of NH_4^+ breakthrough probably represents a very stringent target for practical use of zeolites in removing NH_4^+ from wastewaters. The operating NH_4^+ removal capacity of zeolites at the breakthrough (i.e., breakthrough NH_4^+ capacity) was determined by means of graphical integration of the area above the breakthrough curve, which was obtained by plotting equilibrium NH_4^+ concentration versus number of BVs passed through zeolite column (Schoeman 1986; Pansini 1996).

Table 3 Composition of synthetic effluent (Klieve & Semmens 1980).

Element	Concentration (g m^{-3})	Compound used: Formula	Compound used: Amount (g m^{-3})
Nitrogen (as NH_4^+)	14	NH_4Cl	53.5
Sodium (Na^+)	29	NaCl	73.7
	29	$NaHCO_3$	106.0
Potassium (K^+)	12	KCl	22.9
Magnesium (Mg^{2+})	8	$MgSO_4$	39.6
Calcium (Ca^{2+})	34	$CaCl_2.2H_2O$	124.7
Phosphate (as PO_4^{3-})	8.5	KH_2PO_4	37.3
pH	7.5		
Chemical oxygen demand (COD)	91		

Table 4 Operating conditions of zeolite-packed leaching columns used in the flow-through study.

Parameter	Fast rate (15.9 mm min^{-1})	Slow rate (0.47 mm min^{-1})
Diameter (cm)	2.5	2.5
Internal surface area (cm^2)	4.9	4.9
Length (cm)	60	60
Packed height (cm)	30.5	50
Bed volume (cm^{-3})	150	245.4
Weight of zeolite (g $column^{-1}$)		
Clinoptilolite-coarse		164
Clinoptilolite-fine		147
Mordenite-coarse	150	248
Mordenite-fine	158	258
Influent flowrate		
mm min^{-1}	15. 89	0.47
mm h^{-1}	953.4	28.2
ml min^{-1}	7.8	0.23
ml min^{-1} g^{-1} zeolite		
Clinoptilolite-coarse		1.40×10^{-3}
Clinoptilolite-fine		1.56×10^{-3}
Mordenite-coarse	0.052	9.27×10^{-4}
Mordenite-fine	0.049	8.91×10^{-4}
Zeolite bed volume (BV)$hour^{-1}$	3.12	0.056
Contact time (h BV^{-1})	0.32	17.78
Pore volume (cm^3)		
Clinoptilolite-coarse		152
Clinoptilolite-fine		179
Mordenite-coarse	77	127
Mordenite-fine	84	137

Analytical techniques

Both influent and effluent samples were refrigerated at 4°C until analysis for NH_4^+, generally within 24 hours. Ammonium as nitrogen (NH_4-N) was determined using an Orion Model 95-10 ammonia selective electrode connected to an Orion Model

Table 5 Characteristics of the wastewaters used in the flow-through study. Synthetic composition as shown in Table 3, except that 382 g m^{-3} NH_4Cl was added to provide 100 g NH_4-N m^{-3}. * not analysed.

Wastewater	NH_4-N (g m^{-3})	PO_4-P (g m^{-3})	pH	COD (g m^{-3})	SS (g m^{-3})
Piggery	100.4	40.8	7.7	476	115
Dairy	99.8	21.9	7.7	518	190
Synthetic	100.0	8.5	7.5	*	*

701 digital pH/mV meter (APHA 1989). Full recalibration (1, 10, and 100 g NH_4-N m^{-3} standards) was carried out after every 30 analyses. In addition, duplicates of two effluent samples and duplicates of two NH_4Cl standards (1 and 10 or 10 and 100 g NH_4-N m^{-3}, depending on the NH_4^+ range in the collected wastewaters) were analysed between every 10 unknown samples as a drift check and a check against the calibration curve, respectively.

Wastewaters were analysed within 24 hours of collection, using standard methods (APHA 1989, unless otherwise stated), for: pH (Radiometer 26 meter and combination electrode), conductivity (Radiometer CDM 83 meter with readings corrected to 25°C), 5-day biochemical oxygen demand (BOD_5; APHA method 5210 B), suspended solids (SS; GFC filter, gravimetric; APHA method 2540 D), phosphorus present as phosphate (also termed dissolved reactive phosphorus (DRP; ascorbic acid method; APHA method 4500-P E), chemical oxygen demand (COD; closed reflux, colorimetric; APHA method 5220 D), and chloride (Cl^-; APHA mercuric nitrate method 4500-Cl C). Sulphate in wastewaters was determined colorimetrically at 670 nm wavelength, using the method described by Johnson & Nishita (1952).

Total calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) in wastewaters was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) after digestion with concentrated nitric acid (APHA method 3120 B).

Statistical analyses and modelling

Analysis of variance between NH_4^+ removal performance of zeolites (expressed as % of NH_4^+ inputs from wastewaters or synthetic solutions) and factors affecting this NH_4^+ removal performance (e.g., wastewater type, wastewater NH_4^+ concentration, and zeolite particle size) was conducted using Data Desk statistical software (Velleman 1997) to compare batch adsorption data obtained from different zeolite and wastewater treatments, and to establish the relative importance and interactions of these factors on NH_4^+ removal performance using the F-test and probability (P) values.

Ammonium removal data obtained after shaking zeolite with NH_4Cl solutions containing 14–750 g NH_4-N m^{-3} were fitted to the following Langmuir equation:

$$x/m = abC_e/(1+bC_e) \quad (1)$$

where x/m is the mass of NH_4^+ adsorbed per mass of zeolite (g NH_4-N kg^{-1}); a is the maximum NH_4^+ adsorption capacity of 1 kg of zeolite (g NH_4-N kg^{-1}); b is a Langmuir energy constant (affinity index) or binding strength (m^3 g^{-1} NH_4-N), and C_e is the NH_4^+ concentration in equilibrium solution (g NH_4-N m^{-3}).

Linear regression analyses between maximum Langmuir NH_4^+ adsorption value (a) and zeolite physico-chemical properties were conducted to assess zeolite properties that are likely to influence the NH_4^+ adsorption capacity of these zeolites.

RESULTS

Zeolite physical and chemical characteristics

Zeolite physical and chemical characteristics are reported in Table 1. The Si:Al ratio and Si:(Al + Fe) ratios in both zeolites were similar (3.8–5.0 and 4.0–5.3, respectively) to those reported for other New Zealand (Sameshima 1978) and overseas clinoptilolites and mordenites (Sheppard 1971; Hawkins 1983; Czaran et al. 1988; Beler-Baykal et al. 1996). The results confirmed overseas findings that the mordenite has a lower K content but higher Ca and Na content, and higher Na:K ratios than clinoptilolite.

Both coarse and fine mordenites had higher LOI than moisture content, suggesting that any water moisture trapped within the mordenite crystalline lattice (Czaran et al. 1988) is not released at 105°C but readily removed at 550°C. The LOI content, pH values, and porosity of the studied zeolites were within the range reported in the literature (e.g., Czaran et al. 1988; Olah et al. 1988; Bernal & Lopez-Real 1993). However, the studied zeolites had a lower water holding capacity (WHC) and cation exchange capacity (CEC) than overseas zeolites (WHC and CEC of 133–170% and 150–200 me. %, respectively; Koon & Kaufman 1975; Klieve & Semmens 1980; Schoeman 1986; Bernal & Lopez-Real 1993; Boettinger et al. 1995; Booker et al. 1996). The lower WHC of the studied mordenite compared with the studied clinoptilolite suggests that the former may have limited use as a water-absorbing (hydrophilic) material compared with the latter.

The mordenite had a higher bulk density (BD) than the studied clinoptilolite (Table 1) and overseas mordenites (e.g., BD of 0.53–0.98 g cm^{-3}; Klieve & Semmens 1980; Bernal & Lopez-Real 1993). The higher BD of the studied mordenites means that