The Influence of Zeolite Type A on Metal Concentrations in Water and Waste Water

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ABSTRACT

Investigations were made to determine the removals of calcium, copper, chromium, nickel, lead and zinc from water and waste water samples by different concentrations of zeolite type A and with zeolite type A forms where sodium had been partially exchanged for calcium. Metal concentrations were determined after a range of different treatments such as filtration, sedimentation in columns and centrifugation.

The results indicated that the rate of removal of calcium hardness from samples was a function of the calcium hardness present in the samples. High concentrations of zeolite removed all the metals except chromium from water, but only lead, zinc and cadmium from synthetic waste water samples. In water samples containing cadmium, nickel, copper and zinc, an increase in the calcium exchanged for sodium in the zeolite resulted in a decrease in the percentage of nickel removed from suspension on mixing. At lower environmental concentrations, zeolite type A had no effect on the removal of metals from raw waste water samples.

INTRODUCTION

The possible role of detergent phosphorus in eutrophication (1) has stimulated the search for nonphosphate detergent builders (2,3). Zeolite type A, a synthetic aluminosilicate, is currently being assessed as a substitute for the phosphate detergent builders (3-5).

In contrast to the builders which chelate ions from solution, zeolite type A removes calcium and, to a lesser extent, magnesium from solution by ion exchange (4). For the particle sizes used in detergent formulations, the maximum calcium exchange capacity of zeolite is approximately 200 mg CaOg^{-1} zeolite at 90 C, but only 150 mgg^{-1} at 20 C when no sodium is present in solution (6). The detergent formulations containing zeolite type A are manufactured such that, by the end of a washing program, only 20 to 30% of the calcium exchange capacity of the zeolite has been exerted (6).

The thermodynamic behavior of zeolite type A has been studied and exchange isotherms with metals have been reported (7); the selectivities for cations have been placed in the following order (8): $Ag^+ > Cu^{2+} > H^+ > Zn^{2+} > Sr^{2+} > Ba^{2+} > Ca^{2+} > Co^{2+} > Au^{3+} > K^+ > Na^+ > Ni^{2+} > NH_4^+ > Cd^{2+} > Hg^{2+} > Li^+ > Mg^+$, which generally agrees with the selectivities for divalent ions reported elsewhere (9). Since the ion exchange reactions are kinetically controlled, these thermodynamic selectivities may be of secondary relevance and it is the selectivities at the low concentrations of metals found in the environment that are important. The order of selectivities at low environmental concentrations of ionic metal has been reported (8) as $Pb^{2+} > Ag^+ > Cu^{2+} >> Cd^{2+} > Zn^{2+} >> Co^{2+}, Ni^{2+}, Mn^{2+}$.

The ion exchange has also been reported (8) to increase with decreasing water hardness, increasing temperature, increase in the pH of the solution, increasing concentration of aluminium silicate and decreasing concentration of heavy metal. At a concentration of the sodium form of zeolite type A of 100 mgl^{-1} and 1 mgl^{-1} each of lead, silver, copper, cadmium and zinc in a solution of hardness 110 mgCal^{-1} at 23 C and pH 7, only lead and silver were completely removed after 1 h; after 24 h, 50% of the copper, 25% of the cadmium and 10% of the zinc were removed (8). The values reported above were obtained in aqueous solutions.

After use in the wash process, the waste wash water containing the zeolite would enter the public sewers and be conveyed to a waste water treatment works. The removal of zeolite type A from waste water during primary sedimentation and biological treatment has been demonstrated in a full-scale treatment plant and removal has also been observed in a package plant (10,11). The influence of zeolite type A on metal removal in a laboratory-scale activated sludge simulation treating synthetic sewage has been investigated (5) and no adverse effects have been found.

Estimated concentrations of zeolite type A expected in domestic waste waters after use of detergents containing zeolite type A vary, depending on the detergent formulation, water hardness and the volume of water. Concentrations as high as 50 mgl^{-1} zeolite type A in hard water areas of West Germany (10) and as low as 10 mgl^{-1} in the USA (11) have been predicted.

It is important to study the ion exchange behavior of zeolite type A with metals in the presence of more complex matrices than those present in wash water, since zeolite type A may influence metal concentrations reaching surface waters after waste water treatment.

MATERIALS AND METHODS

Samples Used

Calcium hardness was determined in zeolite treated and control samples of London tap water and synthetic, raw and settled sewages. In other studies percentage metal removals were estimated in control and zeolite treated samples of London tap water, distilled water, and synthetic and raw sewages. The composition of the synthetic sewage sample (Table I) resembled that used in the study of the biodegradation of surfactants (12). Raw and settled sewages were obtained from two water pollution control works in the London area operated by the Thames Water Authority (Hogsmill Valley and Mogden).

Estimation of Calcium Hardness

The calcium hardness of filtered samples was determined using ethylenediaminotetracetic acid (EDTA) (13).

Exchange of Calcium for Sodium in Zeolite Type A

The sodium form of zeolite type A obtained from Henkel KGaA (Düsseldorf, W. Germany) was exchanged for calcium in distilled water by stirring 3 g of zeolite with the required amount of calcium chloride (fused GPR) for 30 min at 20 ± 1 C; 0.29 g, 0.59 g, 0.88 g and 1.18 g, respectively, were used to obtain 25%, 50%, 75% and 100% calcium exchanged zeolite type A.

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TABLE I

Synthetic Sewage Composition

Constituent	Reagent grade	Concentration gl^{-1}
Lab Lemco (meat extract)	Oxoid L29	0.234
Bacteriological peptone	Oxoid L34	0.156
Sodium chloride (NaCl)	GPR	0.009
Calcium chloride ($CaCl_2$)	GPR	0.005
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	"AnalaR"	0.002
Ammonium chloride (NH_4Cl)	GPR	0.072
Potassium dihydrogen orthophosphate (KH_2PO_4)	"AnalaR"	0.006

Addition of Zeolite Type A to Samples for the Estimation of Calcium Hardness or for Centrifugation

The sodium form or calcium exchanged form of zeolite type A was added to 11 samples which were stirred for 30 min at 20 ± 1 C.

Centrifugation of Samples

Centrifugation at 8000 × g for 10 min (MSE Hi Spin 21 Centrifuge) was used to separate the zeolite and other particles from sample suspensions. The supernatants were removed, acidified to 1% v/v with "AnalaR" nitric acid and analyzed for their metal content.

Addition of Samples to Sedimentation Columns

Sedimentation tests were made using two Perspex columns, each 2.7 m high with an internal diameter of 150 mm. Sampling points were provided at 300 mm centers. The samples were drawn off by means of 2.3-mm-diameter stainless steel tubes inserted through ports into the liquid immediately prior to sampling and withdrawn after sampling.

The columns were filled from the bottom by a centrifugal electric pump (C25, Charles Austen Pumps, Weybridge, UK) drawing from 60-ℓ tanks in which the samples were kept in suspension by electrically driven stirrers until the test commenced.

Zeolite type A was added to raw sewage to a nominal concentration of 30 mgl^{-1}; the suspensions were stirred until they attained room temperature and then pumped into the columns. The filling of the columns required approximately 1 min.

Addition of Metals

Six of the so-called "heavy" metals were studied. Cadmium, nickel, lead and zinc were added to the different samples as a solution of "AnalaR" grade nitrate salts. Copper and chromium ions were obtained in solution from copper metal and potassium chromate. Lead and chromate were omitted from some of the studies in order to avoid precipitation of lead chromate. Since the raw sewage samples contained metal ions, no metals were added to them.

Metal Analyses

A rapid flameless atomic absorption method was used for the analyses of all samples. The suitability of the method for samples of this type has been previously reported (14). The zeolite concentration was determined as aluminium using a flameless atomic absorption method (15).

RESULTS

Removal of Calcium Hardness in Water and Sewage Samples by Zeolite Type A

The sodium form of zeolite type A (3 g) was added to the samples of tap water, synthetic sewage, and raw and settled sewages. The calcium hardness of all four samples was determined. The average changes in the removal of calcium hardness with time are presented in Figure 1. The time taken for the removal process to reach equilibrium, the initial and final calcium concentrations and the percentage hardness removed are presented in Table II. This shows that in all the samples more than 99% of the calcium hardness present was removed by the zeolite, although the initial calcium hardness concentrations of the samples differed from each other. It can be seen that the time in which an equilibrium was reached was faster for the raw and settled sewage samples (Fig. 1), which had a lower calcium hardness than the other two samples.

Removal of Metal Ions from Distilled Water by Zeolite Type A

A solution containing cadmium, copper, nickel and zinc ions was mixed with 3 g each of 25%, 50%, 75% and 100% calcium exchanged zeolite to give nominal concentrations of 1 mgl^{-1} of the metal ions. Samples were centrifuged and the supernatants analyzed for their metal content. The actual metal concentrations and the percentage metal removals were calculated from the initial and final concentrations in the supernatants (Table III). It can be seen that the removal of nickel was the only one to change significantly with an increase in the degree of exchange. Its removal decreased from 100% when 25% calcium exchanged zeolite was added and to 45% when 100% calcium exchanged zeolite was added.

Removals of Metal Ions from Tap Water and Synthetic Sewage by Zeolite Type A

Zeolite type A (3 g) was mixed with tap water and synthetic sewage each containing cadmium, chromium, copper, nickel, lead and zinc ions at nominal concentrations of 0.1 mgl^{-1}, 1 mgl^{-1}, 1 mgl^{-1}, 1 mgl^{-1} mgl^{-1} and 5 mgl^{-1}, respectively, for each metal. Exchanges were also performed in the absence of lead. The percentage removals of the metals were calculated from the initial metal concentrations determined by flameless atomic absorption spectrophotometry and the metal concentrations obtained after centrifugation. The average initial metal concentrations and metal removals are presented in Table IV. It can be seen that the presence or absence of lead had no effect on the removals of the other metal ions. No chromium was removed from the tap water and synthetic sewage suspensions. More than 80% of the nickel was removed from the tap water suspension and no nickel was removed from the synthetic sewage suspension. Removal of copper was greater than 95% in the tap water suspension and less than 10% in the synthetic sewage suspension. More than 95% of the cadmium, lead and zinc ions were removed from both samples.

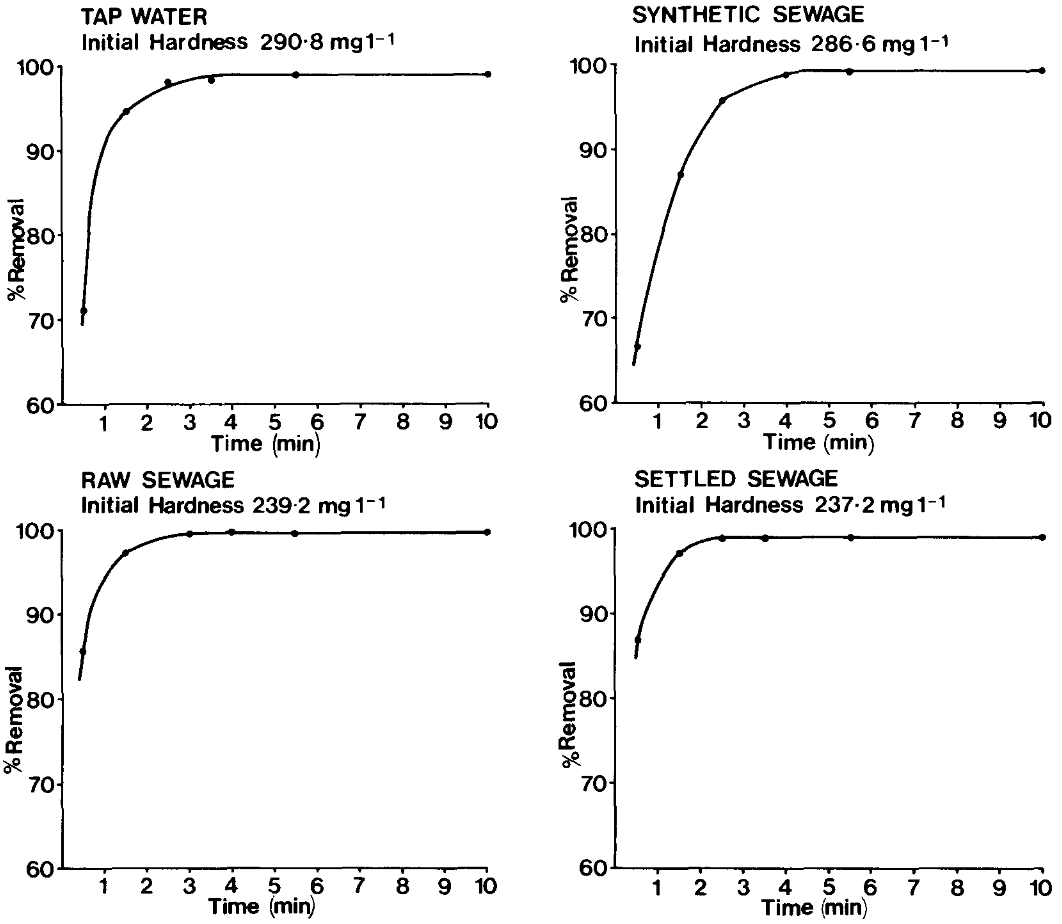

FIG. 1. Percentage removal of calcium hardness (as mgl^{-1} $CaCO_3$) from tap water and synthetic, raw and settled sewages.

Effect of Zeolite Type A on Metal Removal during Sedimentation

Zeolite type A was added to two different raw sewage samples taken from the Hogsmill Valley Water Pollution Control Works (Thames Water Authority). The suspended solids concentrations before addition of the zeolite were 362 and 389 mgl^{-1}. The initial concentrations of zeolite, as determined by flameless atomic absorption spectrophotometry after its addition to the raw sewage samples, were 26 and 31 mgl^{-1} respectively. Two sedimentation columns were used for each raw sewage sample, one being used as a control to which no zeolite was added. Samples were removed from the 300 mm and 900 mm sampling ports. Metal analyses were performed and the average concentrations of samples from the two ports were taken as being representative of the concentrations to be expected in settled sewage.

The percentage removals of metals from sewage in the presence and absence of zeolite after 30, 60, 120 and 180 min settling are presented in Table V along with the initial concentrations. There appeared to be no significant difference between removals of metals with and without zeolite type A.

There was an increase in removals with time for all metals. After 180 min, the highest removal was that of lead, followed by those of chromium, zinc, copper, cadmium and nickel, respectively.

Effect of Zeolite Type A at Different Degrees of Exchange on Metal Removal from Raw Sewage

The sodium form of zeolite type A and 25% calcium exchanged zeolite were added from a stock suspension of 3 gl^{-1} zeolite to two different raw sewage samples from the Mogden Water Pollution Control Works (Thames Water Authority) to give final concentrations of 22 mgl^{-1}. The initial concentrations of metals in the raw sewage samples

TABLE II

Removal of Calcium Hardness from Tap Water, Synthetic, Raw and Settled Sewages by Zeolite Type A

Sample (1)	Initial calcium hardness mgl^{-1} $CaCO_3$	Residual calcium hardness mgl^{-1} $CaCO_3$	% Calcium removed from sample	Time taken to achieve equilibrium
Tap water	290.8	2.1	99.3	5.0
Synthetic sewage	286.6	2.1	99.3	5.0
Raw sewage	239.2	1.0	99.6	3.0
Settled sewage	237.2	2.1	99.1	2.5

are presented in Table VI; the average percentage removals of metals in samples and controls were determined after centrifugation. There was little difference between the percentage metal removals in the unexchanged samples and the 25% calcium exchanged samples; the differences were all less than 10%. A comparison of metal removals in control samples with removals in treated samples indicated there was little difference between the two samples. Only the removals of lead exhibited a difference of greater than 10%. The highest removal was that of lead, followed by those of copper, cadmium, chromium, zinc and nickel, respectively.

DISCUSSION

Zeolite type A is used to remove calcium hardness from wash waters. It has been shown that hardness is removed from municipal sewage by zeolite (3). The work presented here demonstrates that the removal of calcium hardness by zeolite type A which occurs in raw synthetic and settled sewages as well as tap water reaches a rapid equilibrium and probably depends on the hardness of the sample.

It has already been reported that ion exchange occurs with metal ions other than calcium and magnesium (3,8) and that this exchange is dependent on various factors, including water hardness, temperature, and zeolite and metal ion concentrations (8).

Zeolite present in waste wash water would be expected to be in a partially calcium exchanged form (6,16). It would appear that for the metals studied, even at the maximum theoretical degree of exchange of zeolite in distilled water, metal ions are completely removed from suspension, except for nickel. Thermodynamic data on ion exchange (17) indicate that the nickel form of zeolite type A is not as stable as other metal forms of zeolite type A.

When waste wash water reaches the sewer, it mixes with other waste water containing metals and inorganic and organic compounds. The metal removals obtained in tap water and synthetic sewage show that at the high concentrations of zeolite used, the metals are almost completely removed from tap water within 30 min of contact. The exception as shown in the work reported here was chromium. Zeolite type A has a very low affinity for multivalent ions (7) and as hexavalent chromium was used in the studies, the absence of any removal was to be expected.

TABLE III

Removals of Metal Ions from Distilled Water by Zeolite Type A at Different Degrees of Calcium Exchanged for Sodium

Metal	Initial metal concentration mgl^{-1}	Removal % degree of exchange			
		25	50	75	100
Cadmium	1.02	100	99	99	99
Copper	1.0	100	99	100	100
Nickel	1.01	99	86	68	45
Zinc	1.03	100	95	99	99

TABLE IV

Removals of Metal Ions from Tap Water and Synthetic Sewage by Zeolite Type A with and without Lead

Metal	Initial metal concentration mgl^{-1}	Tap water without lead	% Removals with lead	Synthetic sewage without lead	% Removals with lead
Cadmium	0.104	99	100	99	100
Chromium	1.03	0	0	0	0
Copper	1.0	97	97	9	5
Nickel	1.02	89	82	0	0
Lead	0.95	–[a]	100	–[a]	100
Zinc	5.1	100	98	100	100

[a] Omitted to avoid precipitation of lead salts.

TABLE V

Removals of Metals during Settling Column Tests in Raw Sewage with and without Zeolite Type A

Metal	Initial concentration mgl^{-1}	% Removal 30 min with zeolite	30 min without zeolite	60 min with zeolite	60 min without zeolite	120 min with zeolite	120 min without zeolite	180 min with zeolite	180 min without zeolite
Cadmium	0.0053	20	22	22	24	23	26	27	29
	0.0062	23	21	26	25	28	26	32	31
Chromium	0.0074	26	27	38	40	50	53	54	56
	0.0104	22	20	33	31	41	42	48	46
Copper	0.13	33	31	40	42	45	45	47	48
	0.23	34	32	41	43	48	49	50	52
Nickel	0.11	6	6	11	11	17	16	23	22
	0.13	7	6	13	12	21	21	28	29
Lead	0.06	44	41	55	54	69	67	70	68
	0.15	42	39	53	51	65	64	66	65
Zinc	0.29	25	29	39	43	44	46	47	49
	0.46	20	22	32	34	39	40	40	42

TABLE VI

Removals of Metal Ions from Raw Sewage by the Sodium Form of Zeolite, 25% Calcium Exchanged Zeolite and in the Absence of Zeolite Type A

	Unexchanged zeolite type A 22 mgl^{-1}			25% calcium exchanged zeolite type A 22 mgl^{-1}	
	Initial concentration mgl^{-1}	Control removal %	Sample average removal %	Control removal %	Sample average removal %
Cadmium	0.0096	85	84	85	89
	0.0069	51	58	51	60
Chromium	0.091	60	69	60	70
	0.139	45	48	45	51
Copper	0.13	91	91	91	95
	0.13	70	73	70	74
Nickel	0.09	33	34	33	36
	0.20	25	21	25	16
Lead	0.072	99	97	81	95
	0.042	80	93	80	87
Zinc	0.92	40	40	40	37
	0.76	25	28	25	31

The low removals of nickel and copper obtained in synthetic sewage are probably the result of the high affinity of these metals for soluble organics and inorganic compounds (18,19). The metal concentrations used in this study were higher than those previously reported for municipal waste waters (20,21), as was the concentration of zeolite used (10,11). At these concentrations lead removals were complete even in the presence of chromium salts with which insoluble lead chromate easily could have been formed at higher concentrations.

Primary sedimentation is more efficient in the removal of some metals from raw sewage than others (20) because some of the metals are in a soluble form, whereas others are in an insoluble form and can therefore settle out of suspension. Chromium removals were therefore observed with raw sewage samples, whereas no removals were observed in synthetic sewage and tap water where the chromium was in solution. The sedimentation process depends on various factors, including metal form, pH and the presence of complexing agents (22). With the addition of zeolite within the range of its expected environmental concentrations, the sedimentation of the metal ions was neither enhanced nor adversely affected to any significant degree. The peak metal removals at the end of 180 min in control and treated samples and the order of removals were as anticipated.

Centrifugation of samples is a more efficient method of separating solids from suspension than sedimentation. Even with this method, no significant difference was observed between percentage metal removals in control and treated samples, with the possible exception of lead, where the improved removal of the metal from suspension in the presence of zeolite type A may have been caused by the zeolite.

These studies were conducted over a period of time sufficient to ensure equilibrium calcium removal. It is possible that longer contact times with the lower concentrations of zeolite type A added to the raw sewage samples may lead to an improvement in the removals of some metals, as was shown by Schwuger et al., in water (8). This may not be the case, however, as raw sewage samples would contain natural and synthetic chelating agents (22), which would compete with zeolite type A for the metals. In these studies zeolite type A had no adverse effects on metal removals from water and waste water samples.

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