Wastewater Treatment Using Lime and Sea Salt Brine

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ABSTRACT. The wastewater treatment process described in this paper is based on utilising sea salt brine as a source of magnesium for coagulation. Sea salt brine, a by-product of table salt (NaCl) production from sea water, is a rich source of magnesium and is relatively free of sodium. Magnesium hydroxide is an effective coagulant in water and wastewater treatment. The precipitation of magnesium in conjunction with lime treatment significantly improves the performance and economics of lime use. The sea salt brine provides a cheep source of magnesium for enhancing lime performance in municipal and industrial wastewater treatment. The process was capable of achieving the following removal results: 76% BOD₅, 71% COD, > 99.9% Faecal Coliform, 90% turbidity, 96% total phosphorus, 98% soluble phosphorus, 96% TSS, 85% filtered colour and 43% TKN. This treatment is highly effective for removing phosphorus, turbidity, colour and pathogens. The treated effluent may be suitable for discharge and reuse for irrigation and industrial applications. The efficient removal of pathogens eliminates the need for effluent disinfection. The process results in a chemically stable and easy to dewater sludge suitable for land application.

While chemically enhanced municipal wastewater treatment has generally been limited to tertiary stages, Ayoub (1994) reported that non-biological, chemically enhanced settling is practised in nearly 90% of all treatment plants in Sweden and Norway. In the two countries, many wastewater treatment plants employ chemically enhanced sedimentation as the only form of wastewater treatment. Odegaard (1989) summarised the performance of 56 plants in Norway treating wastewaters generated by equivalent population (EP) of 2,000-750,000. The plants located near the sea utilise the lime/sea water treatment process. Such plants typically achieved the following removals: 84-90% TSS; 81-85% BOD₅; 71-82 COD; 90-93% total phosphorus; and less than 1,000 coliform count per 100 mL.

Where the main objective is to control phosphorus, turbidity and pathogens, and to produce an effluent suitable for irrigation and marine discharge, physiochemical treatment is considered to be an appropriate wastewater treatment technology for smaller communities (Taylor *et al.* 1994, Gambrill *et al.* 1992, Ayoub 1994, Ferguson and Vrale 1984, Odegaard 1989). Taylor *et al.* (1994) and Gambrill *et al.* (1992) demonstrated that physiochemical treatment using lime attained the WHO guidelines in terms of microbiological safety (less than 1000 faecal coliform per 100 mL and less than 1 nematode egg per litre) for purposes of unrestricted crop irrigation. Odegaard (1989), reporting on the Norwegian experience, concluded that the lime/sea water process is a suitable, low coast technology for coastal communities.

This paper describes the development and performance of the lime/sea salt brine process for municipal wastewater treatment. In addition, the paper compares chemical treatment using lime alone, lime and sea water, and lime and sea salt brine. The developed process posses several advantages over the lime/sea water process and has a definite potential in the area of treatment and reuse of municipal and industrial wastewaters.

Coagulation/Flocculation with Lime and Magnesium

Lime is commonly used in water and wastewater treatment to achieve a number of treatment objectives including: softening; clarification; precipitation of phosphorous; disinfection; and removal of colour, heavy metals and other trace contaminants. Lime reacts with the alkalinity in water and precipitates as calcium carbonate (CaCO₃). Above a pH of approximately 8 to 9, calcium carbonate particles carry a negative charge (Ayoub 1994) which does not promote interaction with the majority of the negatively charged colloidal particles in solution. The negative charge limits the ability of lime treatment to effectively remove turibidity and the contaminants associated with turbidity, such as the residual pathogens and phosphorus containing particles.

Magnesium hydroxide, $Mg(OH)_2$, is an effective coagulant (Leentvaar and Rebhun 1982). Below a pH of approximately 12, the positively charged (Ayoub 1994) magnesium hydroxide particles promote interaction with the negatively charged colloidal particles in solution. The favourable electrostatic interaction

destabilises colloids, promotes flocculation, and improves settling (Leentvaar and Rebhun 1982). Magnesium sources include: magnesium deposits and sea water.

The Lime/Sea Water Treatment Process

Sea water provides a source of Mg (Table 1) for coagulation. Reporting on the Norwegian experience, Odegaard (1989) concluded that the lime/sea water process is a suitable, low cost technology for coastal communities, and summarised the performance of 56 plants in Norway treating wastewaters generated by equivalent population (EP) of 2,000-750,000. The plants located near the sea utilised the lime/ sea water treatment process. Such plants typically achieved the following contaminants removal results: 84-90% TSS; 81-85% BOD₅; 71-82% COD; 90-93% total P; and less than 1,000 coliform count per 100 mL.

Parameter	Sea Water (mg/L)	Solar Salt Brine* (mg/L)			
Mg ²⁺	1350	91,800			
Ca ²⁺	400	30			
Na ⁺	10,500	6,100			
K+	380	19,200			
SO ₄ ²⁻	2760	76,000			
CI-	19,000	239,000			

Table 1. Mineral composition of sea water and the sea salt brine

* Obtained from Central Queensland Salt, a division of Cheetham Salt Limited.

Based on full-scale application in Norway, the typical process would consist of screening, grit removal, sea water and lime addition systems, rapid mixing, flocculation, sedimentation, and a system for sludge recycling (Fig. 1).

The Lime/Sea Salt Brine Treatment Process

Sea salt brine is a by-product of salt production from sea water. Evaporation of sea water results in the mineralisation of sodium chloride and the concentration of magnesium in the brine. The sea salt brine supplied by Cheetham Salt Limited (Australia) contained approximately 91,800 mg/L Mg. Compared with sea water, the

brine is relatively free of sodium and contains a reduced level of chloride. Diluted to a Mg concentration of 1,350 mg/L, which is equivalent to the Mg concentration in sea water the brine contains less than 90 mg/L sodium compared with 10,500 mg/L in sea water. Accordingly, as a source of Mg, the brine results in a significantly smaller increase in effluent salinity and an insignificant increase in sodium (Na⁺) concentration. For example, the addition of 24 mg/L Mg (100 mg/L as CaCO₃) from sea water results in an increase of 186.7 mg/L Na⁺, 49.1 mg/L SO₄²⁻ and 337.8 mg/L Cl⁻, compared with an increase of 1.6 mg/L Na⁺, 19.9 mg/L SO₄²⁻ and 62.6 mg/L Cl– using the brine.



Fig. 1. Lime/sea water chemical treatment plant (Odegaard 1989) (A = Grit Removal; B = Rapid Mixing; C = Flocculation; D = Sedimentation; E = Sludge Recycling).

Experimental Evaluation

Jar test experiments were conducted to study the enhancing effects of sea salt brine on lime treatment. To facilitate sludge volume measurement, one litre Imhoff cones were used instead of the standard beakers. A schematic of the Jar test apparatus is presented in Fig. 2. During each experimental run, the same sea brine dose was added to each of the six cones prior to lime addition. Lime was then added at increasing quantities to the cones. Following lime addition, the wastewater was mixed for 1 minute at 150 rpm then slowly mixed at 25 rpm for 15 minutes to achieve flocculation. After 30 minutes of settling following flocculation, the sludge volume was measured and a portion of the supernatant was siphoned out for water quality analysis. The screened and degritted wastewater was obtained from Fairfield wastewater treatment plant located in Brisbane. The plant treats wastewater mainly from domestic sources. All analytical procedures for TSS, BOD, COD, turbidity, colour, conductivity, TDS, coliform, pH, and total and calcium hardness were according to standard methods (APHA 1992).



Fig. 2. Jar test apparatus.

Results and Discussion

Coagulation using magnesium requires precipitating magnesium hydroxide, $Mg(OH)^2$. To precipitate $Mg(OH)^2$, the pH must be raised above approximately 10.2 to 10.5. The solubility of Mg declines dramatically between pH = 10.5 and 11.3, and above pH = 11.3, the solubility of Mg becomes virtually negligible. The solubility of Mg(OH)² can be described by the solubility product, Equation 1, and the data in Fig. 3.

 $K_s = [Mg][OH]^2$ (1)

where $K_s = 10^{-9.4}$, is the solubility product, [Mg] = magnesium concentration (mole/L) and [OH] is the hydroxyl ion concentration (mole/L). The quantity of Mg(OH)₂ precipitate can be increased by increasing the pH above 10.2 and increasing the quantity of external magnesium dose. The data in Fig. 3 indicate that precipitation started earlier when the external Mg dose increased. Using a relatively large magnesium dose can reduce the pH, and therefore the lime dose, required to precipitate a defined quantity of magnesium. The combination of lime and external magnesium dosages thus requires experimental optimisation.

Turbidity Removal. Effective turbidity removal results in the removal of pathogens and other colloidal particles containing phosphorous, nitrogen and organic contaminants. The effectiveness of the lime/sea salt brine process in removing turbidity was demonstrated by the experimental results presented in Fig. 4. The data indicate that the residual turbidity decreased as the pH increased above approximately 9.5 The residual turbidity was reduced to as low as 2 - 6 NTU and turbidity removal exceeded 85% as the pH increased above 10.5.



Fig. 3. Precipitation of magnesium hydroxide.



Fig. 4. Turbidity removal using lime and sea salt brine.

The precipitation of magnesium hydroxide contributes to effective turbidity removal. The data in Fig. 5 indicate that a minimum quantity of Mg precipitate of approximately 100 mg/L as $CaCO_3$ (24 mg/L as Mg) was needed to reduce the turbidity to below 6 NTU. The results also indicate that precipitating additional quantities of magnesium above 100 mg/L as $CaCO_3$ did not significantly improve turbidity removal.

The data in Fig. 5 also present a comparison of trubidity removal using sea water and sea salt brine as sources of Mg. The turbidity removal results were approximately identical. The addition of sea water increased the salinity and therefore the concentration of the positively charged ions in solution. Ferguson and Vrale (1984) and Odegaard (1989) suggested that coagulation using sea water results from increased magnesium precipitation and from non-specific effects of other ions in the sea water. However, the authors reported, based on experiments carried out by Haugan (1977), that magnesium by itself could duplicate the effect of sea water addition.



Fig. 5. Effect of Mg precipitation on colour, turbidity, and phosphorus removal.

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Phosphorus Removal. Precipitation of soluble phosphorus is essential for effective phosphorus removal. Ferguson and Vrale, (1984) reported that soluble phosphorus was removed to a negligible value using lime precipitation. Also, the precipitation of Mg did not contribute to the removal of soluble phosphorus.

The removal of soluble phosphorus alone does not explain the removal of total phosphorus. The removal of particulate and colloidal matter containing phosphorus, including the precipitated phosphorus particles, enhances total phosphorus removal.

The data in Fig. 6 indicate that the removal of total phosphorus increased as the pH increased. Also, the addition of increasing quantities of Mg did not significantly enhance total phosphorus removal. The data in Fig. 5 indicate that following the turbidity reduction results, a minimum quantity of Mg precipitate of approximately 100 mg/L as CaCO₃ was needed to reduce total phosphorus to below 1.0 mg/L.



Fig. 6. Total phosphorus removal using lime and sea salt brine.

Colour Removal. Lime treatment, combined with magnesium hydroxide precipitation, from either sea water or sea salt brine sources, resulted in significant in colour removal (Fig. 7). Colour was measured using filtered samples after pH adjustment to near neutrality. Colour removal can be attributed to chemical reactions, coagulation and adsorption onto precipitating particles, in addition to possible precipitation of trace colour contaminants. The data in Figures 5 and 7 indicate that colour removal increased as the pH and magnesium precipitation increased reaching a residual colour of approximately 20-30 PtCo units. A minimum magnesium precipitate quantity of approximately 100 mg/L as CaCO₃ (Fig. 5) was needed to reduce colour to below 30 PtCo units.



Fig. 7. Colour removal using lime and sea salt brine.

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Sea Water and Sea Salt Brine as Sources of Magnesium. A comparison of treatment results achieved using the lime/sea water and the lime/sea salt brine processes is presented in Table 2. The removal results achieved using the higher lime dose of 400 mg/L were significantly higher than those achieved using the lower dose of 300 mg/L due to increased Mg precipitation. The removal of specific contaminants reached approximately 76% BOD, 71% COD, > 99.9% Faecal Coliform, 90% turbidity, 96% total phosphorus, 98% soluble phosphorus, 96% TSS, 85% filtered colour, and 43% TKN.

External Mg dose (mg/L)	()	24				48			
Lime [mg/L as Ca(OH) ₂]	0		300		400		300		400	
Parameter	RW	SW	SSB	SW	SSB	SW	SSB	SW	SSB	SW
рН	7.5	7.5	10.9	10.7	11.3	11.2	10.7	10.8	11.1	11.0
Turbidity (NTU)	_	48	21	21	4.7	5	20	17	4.5	4.3
TSS (mg/L)	288	84	44	28	8	8	48	20	8	8
P Soluble (mg/L)	6.02	6.02	0.05	0.07	0.05	0.05	0.07	0.05	0.06	0.06
P Total (mg/L)	9.78	7.87	1.82	1.55	0.39	0.37	1.53	1.39	0.38	0.33
Colour (PtCo)	189	1999	51	48	38	31	57	28	39	43
Faecal Coliform (# 100 mL)	8x10 ⁷	6x10 ⁷	300	1038	20	12	675	1950	25	8
BOD (mg/L)	260	155	93	78	66	53	88	102	75	63
COD Soluble (mg/L)	182	182	154	166	122	141	158	170	148	142
COD Total (mg/L)	580	247	230	183	212	185	195	190	180	165
TDS (mg/L)	1013	1070	1110	1990	1160	2020	1340	2910	1290	2960
Conductivity (mS/cm)	1.36	1.36	1.41	2.46	1.47	2.49	1.68	3.56	1.63	3.61
Sludge Volume (mL/L)	30	30	39	38	80	74	48	48	90	97
TKN (mg/L)	52	47	32.5	30.0	32.5	29.1	31.4	30.2	28.0	30.2

Table 2. Comparison of the lime/sea salt brine and lime/sea water processes

RW = Wastewater; SW = Settled wastewater; SSB = Sea Salt Brine; SW = Sea Water

The results confirmed the following differences between using sea water and the sea salt brine as sources of magnesium:

1. for an equivalent Mg dose, the required volume of sea water was approximately 70 times higher than the volume of the sea salt brine; and

2. a significantly higher increase in effluent salinity, mainly contributed by sodium and chloride, resulted from adding sea water compared with using the brine.

Other Considerations. The lime/sea salt brine process is efficient and reliable for removing turbidity, total phosphorous, pathogens, and colour. The efficient removal of pathogens eliminates the need for effluent disinfection. The process results in a chemically stable and easy to dewater sludge. The alkaline sludge and effluent are suitable for land application, providing special benefits for neutralising acidic soils.

The major disadvantages of the process when used for municipal wastewater treatment are the high residual pH, high sludge production, and incomplete removal of soluble BOD₅ and TKN. High pH wastewaters typically require neutralisation before discharge. When marine discharge is intended through an outfall diffuser, the effluent may not require neutralisation. Ferguson and Vrale (1984) calculated that an effluent with a pH = 11 can be readily neutralised to a pH = 9 by dilution with 15-20% sea water in the immediate vicinity of the diffuser jet. Effluent neutralisation may be required for other discharges and specific applications and can be achieved through recarbonation or mineral acid addition. Bayley and Cooper (1981) confirmed that lime assisted primary sedimentation effluents were treated satisfactorily in uniformly mixed activated sludge plants where the oxidation of carbonaceous material and ammonia produced sufficient carbon dioxide and nitric acid to neutralise the alkalinity.

Potential Process Applications

The lime/sea salt brine process should be considered to enhance lime treatment in industrial and tertiary treatment applications and wastewater reuse for industrial processing. The process is useful for transient communities that experience extreme variations in flow and composition such as tourist areas and military camps. With proper optimisation resulting in low turbidity and pathogens content, the effluent may be suitable for irrigation. The effluent is also suitable for marine discharge from small communities when the emphasis is to remove phosphorus, turbidity, and pathogens, rather than achieving near complete removal of BOD.

Conclusion

1. The lime/sea salt brine process achieved the following removal results: 76% BOD, 71% COD, > 99.9% Faecal Coliform, 90% turbidity, 96% total

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phosphorus, 98% soluble phosphorus, 96% TSS, 85% filtered colour and 43% TKN.

- 2. Precipitation of approximately 24 mg/L Mg was required to achieve the optimum treatment results. Precipitation of additional Mg quantities did not significantly improve treatment.
- 3. The process has a wide range of potential applications for treating industrial and municipal wastewaters.
- 4. The lime/sea salt brine and lime/sea water processes gave comparable treatment results. The major differences were the following:
- for an equivalent Mg dose, the volume of the sea water was approximately 70 times the salt brine volume; and
- the salinity of the final effluent resulting from sea water addition was approximately double the salinity resulting from using the brine.

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تعتمد طريقة معالجة المياه العادمة والمقدمة في هذا البحث على إستخدام ماء البحر مركز الملوحة كمصدر لمعدن المغنيسيوم لتخثير الملوثات ومن ثم ترسيبها . ويعتبر ماء البحر مركز الملوحة مصدراً غنياً للمغنيسيوم وتتم المعالجة بإضافة ماء البحر مركز الملوحة ومن ثم ترسيب المغنيسيوم كهيدروكسيد المغنيسيوم بإستخدام الجير .

ويعتبر هيدروكسيد المغنيسيوم مادة فعالة لتخثير الملوثات في المياه العادمة ، ويزيد ترسيب هيدروكسيد المغنيسيوم بإستخدام الجير فعالية معالجة المياه البلدية والصناعية .

وبإستخدام هذه التقنية فقد تم إزالة الملوثات المختلفة من المياه العادمة بنسب تتراح ما بين ٤٣٪ إلى أكثر من ٩ , ٩٩٪ . وبالنسبة إلى المياه المعالجة فإنها قد تكون مناسبة لإعادة الإستخدام لأغراض زراعية أو صناعية . أما المواد المترسبة الناتجة عن المعالجة فبالإمكان تجفيفها بسهولة بهدف إعادة إستخدامها للأغراض الزراعية .