



# AMMONIA REMOVAL BY MAGNESIUM AMMONIUM PHOSPHATE PRECIPITATION IN INDUSTRIAL WASTEWATERS

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## ABSTRACT

In this study, the theoretical basis and limitations of magnesium ammonium phosphate (MAP) precipitation are investigated and experimentally tested for leather tanning industry. The MAP precipitation is applied to leather tanning wastewaters for both segregated flows containing high ammonia concentrations and combined flows. Segregated flow treatment on smaller volumes of wastewater provided an ammonia concentration of down to  $150 \text{ mg l}^{-1} \text{ NH}_3\text{-N}$ . The resulting ammonia concentration of MAP precipitation on combined wastewater is at the level of domestic wastewater which eliminates the need of further nitrogen removal in the biological treatment and provides an effluent quality acceptable for the public sewer. © 1997 IAWQ. Published by Elsevier Science Ltd

## KEYWORDS

Chemical precipitation; leather tanning industry; nitrogen removal; magnesium ammonium phosphate.

## INTRODUCTION

Increasing demand for nutrient control has triggered the efforts to effectively remove nitrogen and phosphorus from wastewaters. Ammonia being a significant form of nitrogen is treated mainly by biological nitrification in domestic wastewaters. Ammonia is not a common parameter in industrial wastewaters, however, in some industries such as leather, fertilizer, inorganic chemicals manufacturing etc. rather high ammonia concentrations are present. Wastewaters from these industries are sometimes not amenable to biological treatment while in some cases conditions for nitrification are not provided unless significant modifications in the biological treatment are made. Consequently, physico-chemical methods of ammonia removal have gained importance as an industrial wastewater pretreatment practice. The most promising ammonia removal is by chemical precipitation as magnesium ammonium phosphate (MAP). The precipitation process is complex and subject to interferences. The studies on this application are limited and theoretical treatment of the subject has not been fully developed.

The important theoretical aspects of MAP precipitation can be summarized as follows.

Although solid phase is accepted as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  the conditions for other hydrates to form may be studied since their solubility products are lower (Söhnle and Garside, 1992). In the MAP precipitation, the pH range of minimum ammonia solubility is given as 8-10 (Zdybiewska and Kula, 1991; Schulze-Rettmer, 1991). However, depending on limiting conditions, solids of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$  and  $\text{Mg}(\text{OH})_2$  should also be considered to select the most appropriate pH. Interfering ions, especially calcium must be accounted for to evaluate  $\text{Ca}_3(\text{PO}_4)_2$  precipitation.

In this study, the theoretical basis and limitations of the MAP precipitation are evaluated and experimentally tested. Synthetic samples as well as actual samples provided from industrial sources are used in the experiments. The study includes the assessment of the form of the solid phase which may be different depending on conditions affecting the solubility. Composition of the solution in terms of interfering ions and ionic strength effects are other important aspects of this application. Calcium is an important interference ion due to its common co-existence in wastewaters. Iron and aluminum used as coagulants in the precipitation are also significant as they precipitate the phosphate. These conditions are evaluated in the leather tanning industry wastewaters considering source-based treatment alternatives as well as combined wastewater treatment. Leather tanning industry is a good example for the treatment of MAP precipitation in that the wastewaters contain a wide range of ammonia depending on the sources, and a high concentration of calcium as well as other potential inhibitory substances. On the other hand, several stages of pretreatment on segregated flows can be practiced. Therefore several alternatives for the application of MAP seem to exist.

## EXPERIMENTAL

### Wastewater characterization

A source-based sample to represent the concentrated wastewater in terms of ammonia is taken from a bovine leather tanning factory as a composite of liming, deliming and bating flows. Another sample is taken from the balance tank of the Istanbul Leather Tanners District central treatment plant which receives the wastewater of leather tanning factories of all types (Sample I). To represent the combined wastewater which has undergone pretreatment a composite sample was prepared. Liming wastewater is first air oxidized to remove sulphide and then recarbonated to remove excess calcium and acidified to pH 3.5 to precipitate proteins, and the supernatant is combined flow proportionally with all other process wastewaters (Sample II). The characterization of the composite samples is given in Table 1.

Table 1 Characterization of combined wastewaters\*

	COD	TKN	$\text{NH}_3\text{-N}$	$\text{PO}_4\text{-P}$	Ca	pH
Sample I	4150	310	200	4.1	305	7.37
Sample II	8535	1055	650	3.9	180	3.50

\* all units in  $\text{mg l}^{-1}$  except pH

### Materials and methods

MAP precipitation experiments are carried out in 500 ml beakers. Mixing is provided with magnetic stirrers. Chemicals addition and initial pH adjustment are under flash-mixing conditions which is followed by slow-mixing with varying duration depending on the experiment. Systems equilibrium is checked by pH monitoring. pH measurements are made with Orion 720 model pH meter and pH is adjusted using either NaOH or  $\text{H}_2\text{SO}_4$ . After the precipitation samples are filtered through 0.45  $\mu\text{m}$  Millipore filter. Catalytic sulphide oxidation is conducted with  $\text{MnSO}_4$  catalyst at the ratio of  $\text{Mn}/\text{SO}_4$ :0.4. Air is supplied through diffusers. Recarbonation is carried out using  $\text{Na}_2\text{CO}_3$  for source-based sample and  $\text{CO}_2$  for composite

Sample II. Synthetic samples are prepared using  $MgCl_2 \cdot 2H_2O$ ,  $NaH_2PO_4$  and  $NH_4Cl$  salts. All chemicals used are analytical grade. All analyses are made according to Standard Methods (APHA, 1989).

### Experimental results

Results of the precipitation experiments at stoichiometric dose ( $NH_4^+/Mg^{2+}/PO_4^{3-} : 1/1/1$ ) with synthetic samples initially contain only  $NH_4Cl$  at several concentration are presented in Table 2. At  $200 \text{ mg l}^{-1} NH_3-N$  the results between pH 8.5-9.3 have the same magnitude of  $NH_3-N$  concentrations. At pH 10 a significant increase in  $NH_3-N$  is observed. At  $1800 \text{ mg l}^{-1} NH_3-N$  the removal is still high, but final concentrations are not meaningful as compared to the results of the first set.

Table 2 Results of MAP precipitation for synthetic samples

$NH_3-N_i$ [ $\text{mg l}^{-1}$ ]	Adjusted pH	Equilibrium pH	$NH_3-N_f$ [ $\text{mg l}^{-1}$ ]	$PO_4-P_f$ [ $\text{mg l}^{-1}$ ]
200	9.0	8.5	24.8	43.2
200	10.0	9.3	23.8	34.6
200	11.0	10.0	67	29.3
1800	9.0	8.5	195	199
1800	10.0	9.6	96	19.3

<sup>i</sup> Initial; <sup>f</sup> after precipitation

Results of experiments conducted on combined wastewaters are shown in Table 3. In general all ammonia removals are above 50 % and mostly over 75 %. In the first set where stoichiometric dosages are used the optimum removal is obtained at pH 9 for Sample I. In these experiments calcium interference ( $305 \text{ mg l}^{-1} Ca$  in the sample) is not compensated with excess dose of phosphate. However, at pH 10 the removal is also satisfactory. Excess dose applications are made for  $Mg^{2+}$  and  $PO_4^{3-}$ .  $PO_4^{3-}$  excess doses are calculated considering calcium phosphate precipitation and an excess of  $PO_4^{3-}$  is added for  $Ca_3(PO_4)_2$  stoichiometry. Excess dose application for the Mg in addition to  $PO_4^{3-}$ , up to 20 % did not provide significant increase in the ammonia removal. Coagulant additions as  $FeCl_3$  and  $Al_2(SO_4)_3$  also did not affect ammonia removal. These results can be anticipated since iron and aluminium hydroxide solubilities are expected to predominate at these pH values. However, in case of  $FeCl_3$  a partial  $PO_4^{3-}$  reduction is observed. The precipitation of Sample II where Mg excess is 30% yielded a very high ammonia removal.

Table 3 Results of MAP precipitation for combined wastewaters

Sample	$Mg^{2+}/NH_4^+/PO_4^{3-}$ [M/M/M]	Adjusted pH	Equilibrium pH	$NH_3-N$ [ $\text{mg l}^{-1}$ ]	$PO_4-P$ [ $\text{mg l}^{-1}$ ]	COD [ $\text{mg l}^{-1}$ ]
I	1/1/1	8.00	7.69	106	200	1325
I	1/1/1	9.00	8.36	36	87.7	1415
I	1/1/1	10.00	9.10	47	56.4	1955
I	1.1/1/1 <sup>1</sup>	9.00	9.05	25	50.6	1315
I	1.2/1/1 <sup>1</sup>	9.00	8.99	40	55.3	1495
I	1/1/1 <sup>1</sup>	9.00	8.92	53	29.8	1360
I	1/1/1 <sup>1,2</sup>	9.00	8.90	50	57.6	1405
II	1.3/1/1.1	9.00	9.00	25	-	6230

<sup>1</sup> Additional  $PO_4$  dose stoichiometric to  $Ca_3(PO_4)_2$ ; <sup>2</sup>  $500 \text{ mg l}^{-1} FeCl_3$ ; <sup>3</sup>  $500 \text{ mg l}^{-1} Al_2(SO_4)_3$

Table 4 represents the changes in wastewater quality in several stages of pretreatment as well as different application dosages and responses to MAP precipitation of all applied source-based samples. Results include all important parameters. In fact the table contains considerable information which warrants a thorough evaluation. However, the main results can be deduced as follows; Precipitation I which is applied to sulphide

oxidized-recarbonated sample with stoichiometric Mg and PO<sub>4</sub> excess corresponding to Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (300 mg l<sup>-1</sup> Ca) yielded very high ammonia removal but excess PO<sub>4</sub> remained at a high concentration. Precipitation II is applied after sulphide oxidation, all with stoichiometric Mg addition and A with no excess PO<sub>4</sub>, B with excess PO<sub>4</sub> corresponding to Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, C with excess PO<sub>4</sub> corresponding to CaHPO<sub>4</sub>. Phosphate concentration is seemed to be controlled by calcium in solution. Ammonia concentrations are, however, higher than expected which can be associated with kinetic limitations due to high concentrations of inhibiting substances.

Table 4 Results of MAP precipitation experiments for source-based sample at pH 8

	NH <sub>3</sub> -N [mg l <sup>-1</sup> ]	PO <sub>4</sub> -P [mg l <sup>-1</sup> ]	Ca [mg l <sup>-1</sup> ]	COD [mg l <sup>-1</sup> ]
Composite	3320	-	-	36700
Sulphide Oxidation	1795	-	4690	29800
Recarbonation	1520	-	300	-
Precipitation I	95	170	105	24340
Precipitation IIA	310	16	1380	13050
Precipitation IIB	245	58	340	16225
Precipitation IIC	150	194	210	19050

## CONCLUSIONS

Experiments on synthetic samples to check theoretical aspects of MAP precipitation yielded results parallel with literature values but they also implied some uncertainties which need to be reconsidered within the context of theoretical evaluation summarized in this study.

The MAP precipitation application in leather tanning industry exhibited a very satisfactory performance. The combined wastewaters of the industry, as a standard treatment practice are subjected to a settling or precipitation prior to discharge to sewer or biological treatment. Therefore aside from chemicals feeding no additional system or equipment is required for MAP precipitation. The resulting ammonia concentration in precipitated combined wastewaters is at the level of that of domestic wastewater which makes it possible to discharge directly to sewer as far as the nitrogen limitation is considered. If a further biological treatment is employed, ammonia concentration corresponds just to the nutrient requirement. Then it eliminates the nitrogen removal i.e. nitrification and maybe nitrification denitrification application in the biological treatment which complicates the system requiring additional residence time, extra oxygen and may cause settling problems. The MAP precipitation is also applicable at the pretreatment step on much smaller volumes and on segregated flows which are also standard practice in leather tanning wastewater treatment. In that case it seems also possible to reach ammonia concentrations of less than 50 mg l<sup>-1</sup> in combined wastewaters.

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