Controlling the acid capacity on wastewater treatment plants

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Summary

Nitrogen and phosphorus removal are important processes within advanced wastewater treatment. For the optimization of ammonium removal (nitrification) the parameter "acid capacity" (also referred to as alkalinity) is of real importance, since the nitrifying bacteria produce acid. If the treated water does not have a sufficiently high acid capacity, the pH can fall below 7.0. In this pH range, both the nitrification and the oxygen utilization rate and the sludge floc formation are severely impaired. The following application note discusses the causes, prediction, determination and removal of acid capacity deficits.

Acid capacity

The term "acid capacity" is usually applied to waters which contain no or very few buffering substances. Waste water, however contains phosphate, ammonium and sulfide ions, organic materials, and calcareous particles. That's why the terms "acid binding capacity" or "alkalinity" of wastewater are used. However, since the term "acid capacity" is more common, it will be used hereafter.

Definition

The acid capacity is defined as the amount of hydrochloric acid that can be added to a certain amount of waste water until a pH of 4.3 is reached (common abbreviation: KS4.3).

Causes of acid capacity deficits in wastewater treatment plants

During the treatment process, organic carbon-, nitrogen- and phosphate-containing wastewater constituents are almost completely mineralized. In all degrading steps acids are formed:

- during nitrification nitric acid is formed (HNO_3)
- during denitrification and carbon degradation carbon dioxide is formed

Acid capacity losses during nitrification

The nitrification proceeds (much simplified) according to the following equations:

Eq. 1: $2\ NH_4^+ + 4\ O_2 \leftrightarrow 2\ NO_3^- + 4\ H^+ + 2\ H_2O$

This process takes place in two steps from NH_4^+ to NO_2^- and further on to NO_3^-. The formation of nitrite or ammonification is carried out by Nitrosomonas bacteria (slowed down at pH less than 7.5). The subsequent nitrate formation is carried out by Nitrobacter bacteria (slowed down at pH less than 5.7). A prerequisite for high turnover rates of the nitrification is that the formed acid ions (H^+ ions) are rapidly absorbed by the bicarbonate equivalents in the wastewater.

Eq. 2: $H^+ + HCO_3^- \leftrightarrow CO_2 + H_2O$ or $2\ H^+ + CO_3^{2-} \leftrightarrow CO_2 + H_2O$

For every mg NH_4-N degraded, 0.14 mmol of acid capacity is consumed. If during nitrification, the resulting nitric acid is not immediately neutralized by buffering substances in the wastewater, the pH

can drop quickly to values below 7.0. The optimum performance of nitrifying bacteria, however, lies in the pH range from 7.5 to 8.5.

Acid capacity generation by denitrification

During the denitrification process the nitrate previously formed by nitrification is reduced to elemental nitrogen:

Eq. 3: $2\ NO_2^{3-} + 2\ H^+ + 2.5\ C_{Org} \leftrightarrow N_2 + H_2O + 2.5\ CO_2$

In contrast to the nitrification process, denitrification consumes acid ions (H^+). Theoretically, the denitrification restores 50 % of the previously consumed acid capacity. The CO_2 formed can, however, again become an acid unless it is sufficiently stripped from the wastewater

Eq. 4: $CO_2 + H_2O \leftrightarrow 2H^+ + CO_3^{2-}$

For every mg of degraded NO_3-N, 0.07 mmol/l of acid capacity is formed.

Problem: Efficient ventilation systems

Due to ever improving aeration devices in modern sewage treatment plants (or aeration with industrial oxygen), the stripping of CO_2 may be reduced due to increased oxygen utilization levels. CO_2 is therefore enriched in the sewer system and subsequently decreases the pH-value.

Acid capacity consumption caused by using acidic precipitants (metal salts)

When phosphate removal is performed using iron and aluminum salts, H^+ ions are released, which may cause a decrease in pH value.

Eq. 5: $Me^{3+} + 3\ H_2O \leftrightarrow Me(OH)_3 + 3\ H^+$

P-elimination with acidic metal salts therefore reduces the acid capacity. 3 moles of acid capacity are consumed per mole of metal ($Fe3^+$ or $Al3^+$).

Example:

Dosage of 50 ml or 72 g of $FeCl_3$ solution per m^3 of wastewater
Acid capacity consumption: about 0.5 mmol/l

Use of alkaline precipitants

Sodium hydroxide solution containing precipitants (E.g. sodium aluminate) generally provide acid capacity:

Eq. 6: $Na_2Al_2O_4 + 2\ PO_4^{3-} + 6\ H^+ \leftrightarrow 2\ AlPO_4 + 2\ NaOH + 2\ H_2O$

The acid capacity gain per kg aluminate is 6 mol. A dose of 100 g aluminate per m3 of waste water increases the acid capacity by 0.6 mmol/l. However, an excess of aluminum may again react to form acid according to Eq. 5, i.e. in practice the total acid capacity gain is often insufficient.

Effects of acid capacity deficits in the treatment process

Effect on nitrification

During nitrification, nitric acid is formed, which should be absorbed immediately after formation by the buffer system within the wastewater. In unfavorable nitrogen/acid capacity ratios the pH can drop to values <4 during nitrification. The following table shows how important a sufficient acid capacity (alkalinity) is:

Table 1: pH-dependence of the nitrification

Measurement values in the aeration	Example 1	Example 2	Example 3
pH	6.4	6.6	7.0
Temperature	8°C	8°C	8°C
O_2 content	1 mg/l	2 mg/l	1 mg/l
N Total in influent	40 mg/l	40 mg/l	40 mg/l
NH_4-N in effluent	12.9 mg/l	5.2 mg/l	1.2 mg/l

At constant temperatures and constant NH_4-N loads, working within the optimum pH range leads to increased nitrification rather than working at pH values <7, even at relatively low O2 levels. This means that the nitrification rate and the oxygen utilization of the nitrifying bacteria in the pH-optimum is significantly higher than at pH values <7.

Effects on the activated sludge quality

On treatment plants that suffer from a lack of acid capacity, hydraulic peaks often cause problems with sludge loss in the effluent. An analysis of activated sludge under a microscope reveals that the sludge consists of many small and light flakes, which are easily carried away by the flow. The reason for the unfavorable sludge structure is the dissolution of calcium carbonate particles from the activated sludge, which represent a preferred growth substrate for the nitrification bacteria.

However, these problems may not be detected by simply measuring the sludge index. This is because the standard determination of the volume of sludge takes place in a settling cylinder in which there is no turbulence (i.e. despite a good sludge index the floc formation might still be negatively impacted). This often means that in the case of sludge loss a significant number of nitrifying bacteria is lost (decreasing sludge age) potentially bringing the complete process to a halt.

Elimination of acid capacity deficits

To act against acid capacity deficits the following measures are possible:

- Commissioning of a denitrification step
- Reduction of the nitrogen load to be nitrified
- Dosage of alkaline chemicals

In most cases, on modern wastewater treatment plants denitrification is already in operation. If acid capacity deficits still prevail, only the last two measures can be considered.

A reduction of the nitrogen load is possible, by stripping ammonium from centrate (about 800-1200 mg NH_4-N) that is produced during sludge thickening and dewatering. However, this method is usually only economical for large sewage treatment plants and / or high nitrogen fluxes.

Dosing alkaline chemicals is used much more frequently. Suitable dosing chemicals are:

- Sodium hydroxide (NaOH)
- Sodium aluminate $Na_2Al_2O_4$
- Sodium carbonate (Na_2CO_3)
- Hydrated lime ($Ca(OH)_2$)

Hydrated lime is by far the cheapest chemical relative to 1 mmol/l acid capacity and is therefore used frequently. The dosage is performed 'dry' directly from the silo or as lime solution. Sodium carbonate is also used to increase the acid capacity, but it is much more expensive than hydrated lime.

Adequate measurement points

In the aeration tank, a sufficiently high acid capacity is necessary because the biodegradation processes can be disturbed by low pH values. The determination of the acid capacity is of particular interest at the sampling points listed in table 2.

Table 2: Sampling points for the determination of the acid capacity

Sampling point	Sample preparation	Recommended min. value
Influent Aeration/ Trickling Filter	WWTP with pre-clarifier: no filtration WWTP w/o pre-clarifier: filtration	Dependent on NH_4-N content: 2-6
Aeration tank	Filtration	> 2
Effluent	None	> 2

When fine particles are still present in the sample at the inflow to the biological stage after primary treatment, they should be included in the determination because they usually dissolve in the course of nitrification, providing acid capacity.

Predicting acid capacity deficits

For the estimation of the expected acid capacity consumption during the treatment process the following formula can be used:

Eq. 7: Acid capacity consumption

$$\delta Ks = 0.035 \bullet (NH_4\text{-}N_{Influent} + \text{Sum } N_{Effluent}) + 0.14 \bullet (\text{Total-}P_{Influent} - \text{ortho-}P_{Effluent})$$

Example: Acid capacity in the influent: 4 mmol/l soft-to-medium hard water

Influent	NH_4-N	50	mg N/l
Effluent	NO_3-N	5	mg N/l
	NO_2-N	0.05	mg N/l
	NH_4-N	1.2	mg N/l
Sum		**6.25**	**mg N/l**
Influent	Total-P	8	mg P/l
Effluent	Ortho-P	1	mg P/l

Insertion into Eq. 7:

$$\delta Ks = 0.035 \bullet (50 + 6.25) + 0.14 \bullet (8 - 1) = 1.97 + 0.98 \approx 3 \text{ mmol / l}$$

With an acid capacity in the supply of 4 mmol/l and an acid capacity consumption of 3 mmol/l a residual acid capacity of 1mmol/l can be calculated. Hence, at least temporary problems in the aeration tank (pH drop, reduced nitrification) can be expected.

Methods to determine the acid capacity

Automated Titration

The determination of the acid capacity can be done using the application kit for the determination of pH and alkalinity on the automated titration system TITRALAB AT1000. The method is stored on the device and simply has to be selected by the user.

Default parameters for the AT1000

The sample size and titrant concentration depend on the quality of the water. Using the application note settings described below with the following parameters:

- V sample = 100 mL
- Burette volume = 10 mL
- Titrant concentration = 0.1 eq/L (corresponding to a 0.1 mol/L HCl solution)

Working ranges

In accordance with the norm ISO 9963-1, the previous configuration with 0.1 eq/L of titrant HCl or H2SO4, 10 mL-burette is done for a Total Alkalinity between 0.4 mmol/L (20 mg/L CaCO3) corresponding to 0.4 mL of titrant 0.1 eq/L and 20 mmol/L (1000 mg/L CaCO3) corresponding to 20 mL of titrant 0.1 eq/L.

For the **best accuracy and reproducibility**, the result range is between 3.5 meq/L or 175 mg/L CaCO3 for 35% of the cylinder 10 mL-burette capacity and 10 meq/L or 500 mg/L CaCO3 for the cylinder 10 mL-burette capacity. With the same conditions, the "experimental" limit corresponding to a titrant volume of 0.5 mL is 0.5 meq/L or 25 mg/L CaCO3.
For **low alkalinity**, below 0.5 mmol/L or 25 mg/L CaCO3 (corresponding to 0.5 mL of titrant 0.1 eq/L), it is recommended to use a low alkalinity method with 0.02 eq/L titrant and 200 mL for sample volume, using the calculation above.
For **high alkalinity**, between 10 mmol/L (500 mg/L CaCO3) and 20 mmol/L (1000 mg/L CaCO3) it is recommended to use smaller sample volumes (less than 50 mL) with the same titrant 0.1 eq/L.

Manual Titration

Hydrochloric acid (HCl, 0.1 mol/l or 0.1N) is added drop-wise to a 100 ml wastewater sample (influent samples are filtered and then processed immediately) until the pH value has reached 4.3 (measured using a pH electrode) or until the previously added methyl orange indicator has changed its color from orange to orange-red.

The amount of added hydrochloric acid in ml is noted. The calculated value corresponds to the acid capacity in mmol HCO_3^-/l.

Example:

In the effluent water of a treatment plant the acid capacity is titrated. 3 ml of 0.1 molar hydrochloric acid are consumed before the color changes. The corresponding acid capacity value is therefore 3 mmol HCO_3^-/l.

Cuvette test

The determination of the acid capacity can also be done using the HACH cuvette test LCK362. Again, for influent samples filtration and a quick analysis is recommended. The cuvette test is based on an indicator that changes color with increasing acid capacity. The resulting color intensity is measured in a spectrophotometer.

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