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Using sulfuric acid (H₂SO₄) for pH adjustment in water treatment

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Abstract

The aim of this paper is to explain the advantages of using sulfuric acid in Qarmat Ali water treatment plant belong to Basrah Oil Company, which produces water for injection into the Rumaila reservoirs. Sulfuric acid is a strong acid providing rapid and effective pH reduction. Maintaining the coagulation pH within the optimum value (6.4) by inject specific value of sulfuric acid to RAW water enhances the clarification performances by reducing the clarified water turbidity to minimum value (5.1). It was preferable for operating at a pH below the saturation pH to prevent the precipitation of minerals such as calcium carbonate which are contributing to blocking the surface filters installed downstream (auto back wash filters) and The clarifiers that cause increased the feed from 500 MBD to 1000 MBD. With a fast and rapid dissociation in Water, Sulfuric acid is an effective and practical way to lower the pH on Qarmat Ali plant which producing in excess of 1,000MBD of export water.

استخدام حامض الكبريتيك المركز للتحكم في قيمة الاس الهيدروجيني للماء المعالج

الخلاصة:

يهدف هذا البحث إلى شرح مزايا استخدام حامض الكبريتيك في محطة معالجة المياه (موقع كرمة علي) التابع لشركة نفط البصرة , والتي تنتج الماء للحقن من مكامن الرميثة. حمض الكبريتيك هو حمض قوي التأثير يوفر تقليلًا سريعًا وفعالًا للاس الهيدروجيني. إن الحفاظ على الاس الهيدروجيني ضمن القيمة الأمثل (6.4) بواسطة حقن كمية معينة من حامض الكبريتيك المركز يعزز أداء التصفية عن طريق تقليل عكورة المياه المعالجة الى اقل قيمة (5.1). من خلال التشغيل عند درجة أقل من الاس الهيدروجيني للتشبع ، فإن هذا يمنع ترسب الاملاح مثل كربونات الكالسيوم التي تسبب انسداد المرشحات (فلتر الغسيل العكسي) الموجودة في المرحلة النهائية للمعالجة وبسبب ذلك استطعنا زيادة الانتاج من 500 MBD الى 1000 MBD (نصف مليون برميل باليوم

الى مليون برميل باليوم). مع الانتاج السريع للماء، يعد حمض الكبريتيك طريقة فعالة وعملية لخفض ألاس الهيدروجيني (زيادة درجة الحموضة) في موقع كرمة علي التي تنتج ما يزيد عن مليون برميل في اليوم من مياه التصدير.

1. Introduction:

pH is an expression of the concentration of Hydronium Ion H_3O^+ at the level of higher or lower than 7. In water treatment pH correction is often required [1], either to decrease or increase to maintain the pH in the selected range. There are many controllers of pH (HCl, CO_2 , Coagulant, H_2SO_4) [2], sulfuric acid is one of the best reagents for the following reasons:

1. It is a strong diacid with a rapid and total dissociation in water [3]. When used at a concentration of 98% requires small volumes required compared to other acids for the same effect (HCl...).
2. It is widely available to be used in many industries and can be delivered at high concentrations (98%).
3. It requires a short contact time to react fully, leading to a fast drop in pH [4]. It can be injected a short distance before the clarifiers.

The optimum coagulation pH will vary depending on which coagulant is used [5]. Aluminium sulphate normally operates at the optimal condition with pH between 5.8 and 6.3 [6]. Not all coagulant need to be in that range depending on the results we want to achieve, the raw water characteristics and the type of coagulant used.

As displayed in Figure (1) from a different site, when pH increased from 6 to 7, the turbidity removal improved with values reducing from 7 to 5.7 respectively. The lowest turbidity of 5.7 is achieved when the pH is 7.0. As the pH increases above 7 the turbidity degrades to reach values in excess of 8. it was observed that the optimum pH was 7.0 as shown in Figure (1) [7].

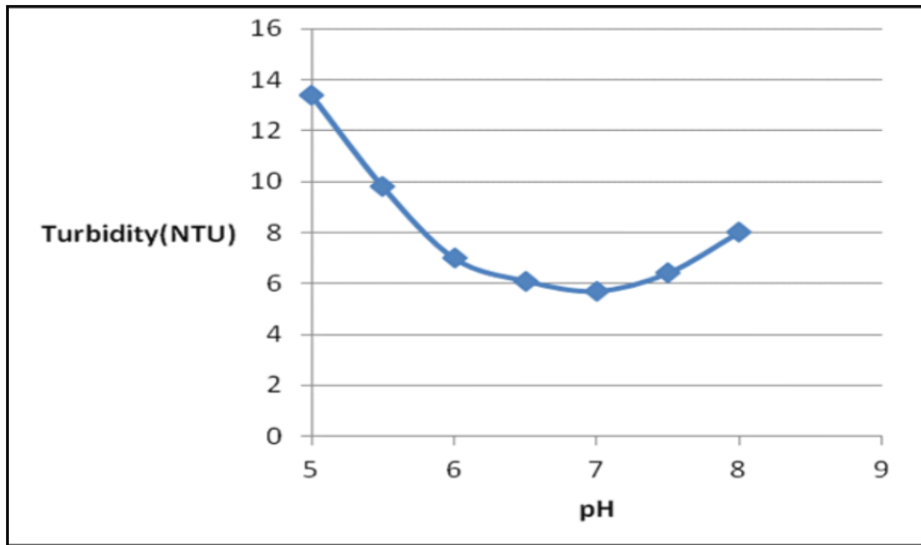


Fig. (1) Effect of pH on turbidity reduction in jar test (different site)

Also as displayed in Figure (2) (from Qarmat Ali site) the same result but a little different, the optimum pH range around 5.75 to 6.4

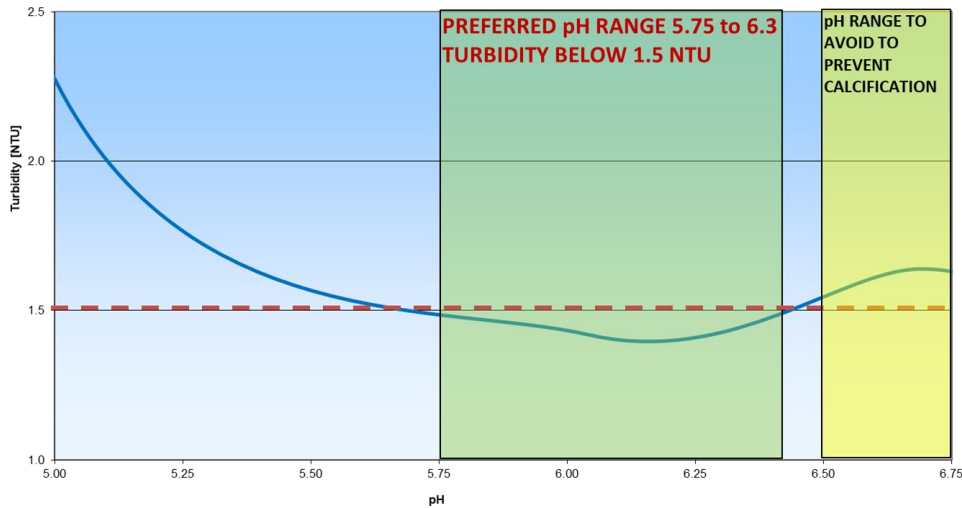


Fig. (2) Impact of pH on clarified water turbidity/jar test in Qarmat Ali.

If pH is higher than the saturation pH, the water will become scaling meaning limestone and will precipitate easily and block disc filter and automatic backwash filters. By maintaining the pH below the saturation pH the calcium carbonate remains in dissolved form as teste on the Qarmat Ali plant.

2. Methods

1- Use sulfuric Acid to maintain the optimum coagulation pH

The value of pH for Qarmat Ali raw water (as measured in BOC LAB in Qarmat Ali) shows the pH is higher than the saturation pH. The latter depends on the water total alkalinity and hardness as shown in Figure (3).

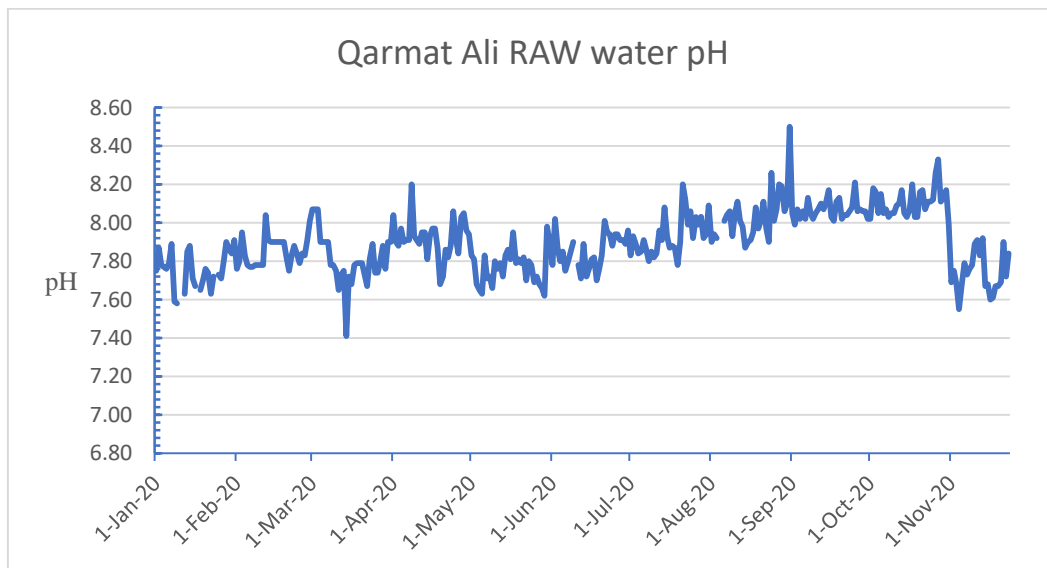


Fig. (3) The value of pH for Qarmat Ali for one year (2020), variation from 7.4 to 8.5

The mass transfer limited CO_2 degassing is the key process in controlling the stream pH [8], the plan of Qarmat Ali water treatment. Figure (4) shows the places where the pH value decrease (acid injection, coagulant and post coagulant dosing) and increase (actiflo, disc filter) due to the degassing of CO_2 . As cascade aeration takes place between the treatment stages the CO_2 is stripped from the water. This displaces the equilibrium which in turn increases the pH.

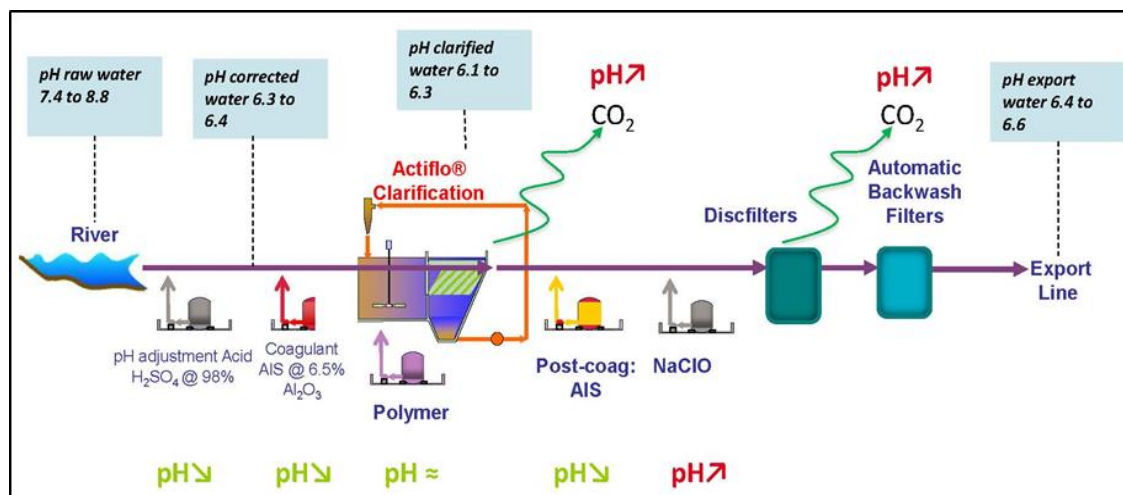


Fig. (4) Changed CO₂ in Qarmat Ali plant

Table (1) The jar test result was taken in 18-jan-2020 by Qarmat Ali lab.

pH	Coagulant dose (mg/l as Al)	Polymer addition(mg/l)	Turbidity (NTU)
6.6	7	0.7	5.50
6.5	7	0.7	5.11
6.4	7	0.7	5.10
6.3	7	0.7	6.67
6.1	7	0.7	7.11

Although the variations are small as Table (1) is consistent with the results obtained throughout the year. The lowest turbidity was achieved for a coagulation pH of 6.4.

From Figure (5) reaching 6.4 pH requires adding 4500 µl of sulfuric acid (2018). This does not take into account the acidification resulting from the coagulant addition, as the water characteristics change the acid demand will vary with values from 10 to 45 liters of commercial acid at 98% per 1,000m³. When the dose required is 4500 µl of acid (diluted 1:100) per liter this means a dose of 45 liters per 1000 m³ of water.

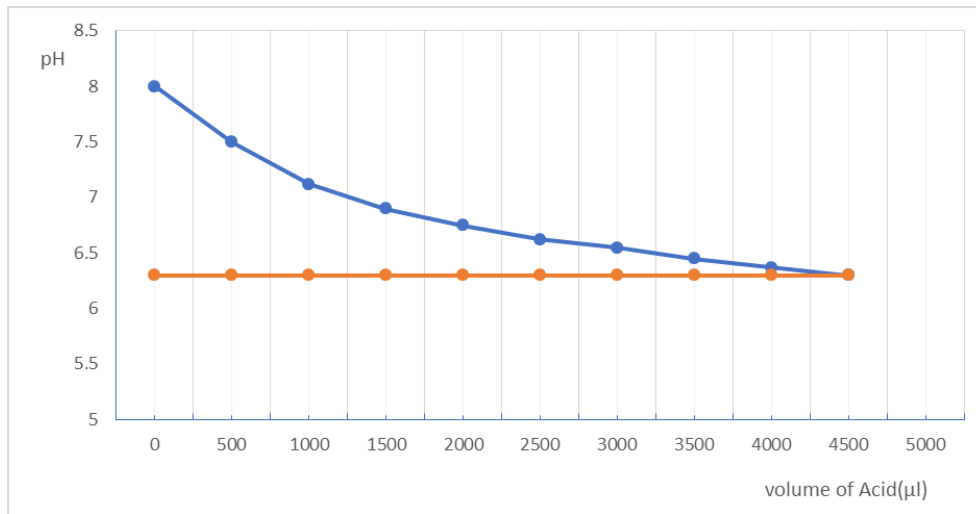


Fig. (5) Diagram between pH and volume of acid, shows at 6.4 pH volume needed =4500 μl

Considering a plant inlet flow of 7,000 m^3/h the total acid injection is $7 \times 45 = 315 \text{ l/h}$

2- Use sulfuric acid to maintain pH below the saturation pH to prevent blockage in micro membrane

The relationship between CaCO_3 solubility and pH in the aqueous solution comparing both simulation and literature at a fixed temperature value of 25°C with a fixed pressure of 1 bar. The pH of the Aqueous solution is at a great importance, as lower values of pH modifies the amount of the CaCO_3 solubility in the aqueous solution (increasing the amount) as displayed in Figure (6) [9].

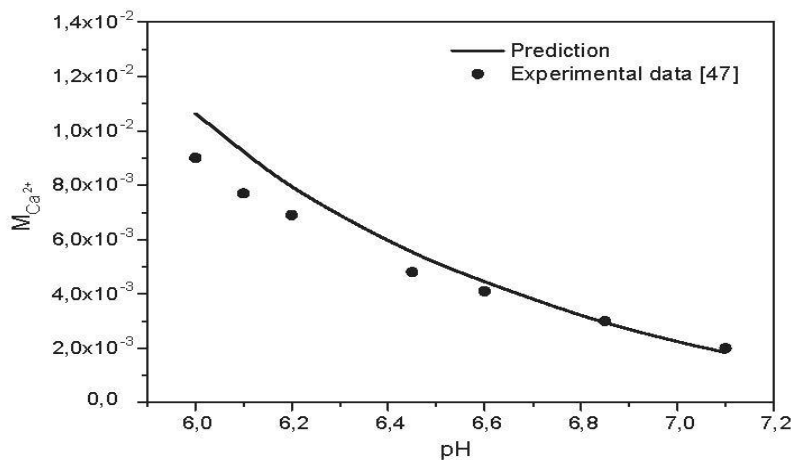


Fig. (6) Effect of the pH on the CaCO_3 solubility at 25°C and 1 bar air pressure.

At high value of pH and above saturation, low solubility of calcium carbonate can lead to deposition [10] on the filtration membrane and cause blockage as the water becomes scaling. As pH value decreases and reaches 6.3 the solubility of calcium carbonate increases, the bicarbonates remain in solution as the water becomes aggressive. The precipitation of calcium carbonate is prevented, reducing the mineral precipitation and additional solid loadings which degrades the filterability capacity.

Operating the plant with no pH correction requires to greatly overdose coagulant to reduce the pH so the pH remains below the saturation pH_s. This degrades the clarified water quality with higher turbidity increases the solids loadings to the disc filters and reduces their filtration capabilities. Without pH correction mineral fouling of the disc filters (10µm) and automatic back wash Filters (5µm) increases rapidly as experienced on the plant. This requires more frequent chemical cleans of the filters to remove the mineral precipitation.

3. Technical and economic viability:

The viability of control the pH value to the optimum coagulation pH is: -

- 1- Reduce the dose of coagulant which would otherwise be higher to achieve the optimum pH. This will saves circa 5 tons of aluminum sulphate per day to seek the same NTU value without using of sulfuric acid.
- 2- Increase the production to 1000 MBD, while the production was 500 MBD without using sulfuric acid.
- 3- No calcium carbonate precipitation causing mineral fouling on the membranes of the disc filters and the auto back wash filters. This also increase the life of the equipment's for circa 2 years.

4. Conclusions:

Sulfuric acid is one of the most effective reagents to reduce the pH, has a rapid reaction time and provides a high level of accuracy when maintaining a target value. It allows controlling the pH value about 6.4 (below saturation pH) by injecting typically between 25 to 45 l/1,000m³ of feed water. By operating at optimum pH, the coagulant effectiveness is maximized and allows clarified water turbidity to be below 1NTU. Maintaining the clarified water below the saturation pH prevents; precipitation of carbon calcium on the filtration membranes. That solves most of the issues of fouling which happened before injecting of sulfuric acid in RAW water, increasing production to 1000MBD.

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