Comprehensive analysis of the treatment plant operation

M Kh Kurbangaleeva and R Kh Giniyatullin

1 Ufa State Petroleum Technological University, Branch in the Sterlitamak, 2, Prospekt Oktyabrya Str., Sterlitamak, 453100, Republic of Bashkortostan, Russia
2 Ufa Institute of Biology, Ufa Federal Research Centre of the Russian Academy of Sciences, 69, Prospekt Oktyabrya Str., Ufa, 450054, Republic of Bashkortostan, Russia

E-mail: mhk2014@bk.ru

Abstract. Comparison of the content of manganese (II) and iron (III) ions in river water and waste water, taking in to account the differentiation of the annual cycle, is carried out. It will allow moving to a comprehensive analysis of the treatment plant. The efficiency checking of the reduction of manganese (II) and iron (III) for a certain period was carried out, taking into account the constant consumption of the volume of water. The efficiency of wastewater treatment from manganese (II) ions is on average 31%, from iron (III) ions - 35%. The results obtained indicate the need for additional measures aimed at minimizing the content of manganese (II) and iron (III) ions in the process waters before the treatment plant. To minimize the content of these ions, it is necessary to select an effective and economic mode for purifying process waters. Purification of process waters from ions of manganese (II) and iron (III) was carried out using the following reagents: potassium permanganate; sodium sulfide; soda ash and sodium phosphate in stage-stage processing; suspensions of strong as well as weak milk of lime and brine sludge. For the purification of process waters from ions of manganese (II) and iron (III), industrial waste was proposed: the suspension of weak lime milk obtained after washing large quenching waste(large green coke - incompletely burned material) and used for transporting small quenching waste (small waste) to the sludge collector channel, and brine sludge suspension.

Wastewater from chemical and petrochemical industries is a source of chemicals of various structures entering water bodies, some of which have high toxicological activity [1,2].

The identification of possible sources of environmental pollution by ions of manganese and iron as well as the development of solutions to minimize their impact on the natural environment without complex additional techniques is an important task at the present time.

It is customary to assess the efficiency of water treatment using either single or averaged input and output data values of the estimated indicator over a certain period. Such estimates are approximate, since they do not take into account the dynamics of changes in the indicator over time. We have evaluated the efficiency of reducing the ions of manganese (II) and iron (III) for a certain period of constant consumption of water volume. The results are shown in table 1.
Table 1. Results of studies of the mass concentration of manganese (II) and iron (III) ions before and after treatment facilities.

| No. of Test | Mass concentration of manganese (II) ions (mg/dm³) | Efficiency, % | Mass concentration of iron (III) ions (mg/dm³) | Efficiency, % |
|-------------|--------------------------------------------------|----------------|-----------------------------------------------|--------------|
|             | Input                                            | Output         | Input                                         | Output       |
| 1           | 0.13                                             | 0.09           | 30.77                                         | 0.90         | 0.54 | 40.00 |
| 2           | 0.11                                             | 0.08           | 23.08                                         | 0.80         | 0.48 | 40.00 |
| 3           | 0.12                                             | 0.08           | 33.00                                         | 0.68         | 0.57 | 17.77 |
| 4           | 0.18                                             | 0.11           | 39.00                                         | 0.80         | 0.60 | 25.00 |
| 5           | 0.21                                             | 0.15           | 29.00                                         | 0.85         | 0.41 | 52.00 |

The efficiency of wastewater treatment from manganese (II) ions is on average 31%, from iron (III) ions - 35%. The totality of the components of the water treatment process causes both regular and stochastic fluctuations in the quality of the waste water. The latter include: technological washing of filters as well as forced operation of the treatment plant. The results obtained indicate the need for additional measures aimed at minimizing manganese and iron in process waters prior to the treatment plant.

To minimize the content of manganese (II) and iron (III) ions, it is proposed to use the following approach:

- selection of an effective cheap method for purifying process waters;
- development of technology with minimal reconstruction of the existing sewerage system.

Iron removal and demanganation of waters are very often solved within the framework of a single technology, taking into account the specifics of extraction of each ingredient. Purification of process waters from ions of manganese (II) and iron (III) was carried out using the following reagents: potassium permanganate; sodium sulfide; soda ash and sodium phosphate in stage-to-stage processing; by means of suspensions of strong and weak lime milk and brine sludge [3,4,5].

Table 2 shows the comparative characteristics of the reagent purification of process waters of from manganese (II) and iron (III) ions.

Table 2. Comparative characteristics of the reagent purification of process waters from manganese (II) and iron (III) ions.

| Purification method | Mass concentration in the original sample | Mass concentration in the sample after purification |
|---------------------|-------------------------------------------|----------------------------------------------------|
|                     | Mn²⁺ (mg/dm³) | Fe³⁺ (mg/dm³) | pH | Mn²⁺ (mg/dm³) | Fe³⁺ (mg/dm³) | pH |
| Permanganate method | 0.26           | 2.3           | 6.2 | < 0.01        | < 0.1         | 6.2 |
|                     | 0.21           | 2.4           | 6.2 | < 0.01        | < 0.1         | 6.2 |
|                     | 0.28           | 3.0           | 6.3 | < 0.01        | < 0.1         | 6.3 |
|                     | 0.29           | 2.5           | 6.4 | < 0.01        | < 0.1         | 6.4 |
|                     | 0.30           | 2.6           | 6.2 | < 0.01        | < 0.1         | 6.2 |
|                     | 0.29           | 2.8           | 6.1 | < 0.01        | < 0.1         | 6.2 |
|                     | 0.27           | 2.7           | 6.3 | < 0.01        | < 0.1         | 6.3 |
| Sulfide method      | 0.27           | 2.3           | 6.2 | < 0.01        | < 0.1         | 8.6 |
|                     | 0.17           | 3.1           | 6.3 | < 0.01        | < 0.1         | 8.7 |
|                     | 0.28           | 2.4           | 6.2 | < 0.01        | < 0.1         | 8.7 |
| Stepwise processing (sodium phosphate + soda ash) | 0.26  | 2.3  | 6.3  | < 0.01 | < 0.1 | 8.6 |
|-------------------------------------------------|-------|------|------|--------|-------|-----|
|                                                 | 0.23  | 2.4  | 6.3  | < 0.01 | < 0.1 | 8.6 |
|                                                 | 0.25  | 2.7  | 6.0  | < 0.01 | < 0.1 | 8.8 |
|                                                 | 0.23  | 2.6  | 6.2  | < 0.01 | < 0.1 | 8.6 |
|                                                 | 0.24  | 2.7  | 6.3  | < 0.01 | < 0.1 | 8.7 |
| Hydroxide method (suspension of strong lime milk) | 0.26  | 2.3  | 6.0  | < 0.01 | < 0.1 | 8.5 |
|                                                 | 0.27  | 3.1  | 6.2  | < 0.01 | < 0.1 | 8.5 |
|                                                 | 0.23  | 2.4  | 5.8  | < 0.01 | < 0.1 | 8.8 |
|                                                 | 0.22  | 2.6  | 5.9  | < 0.01 | < 0.1 | 8.7 |
|                                                 | 0.25  | 2.7  | 6.0  | < 0.01 | < 0.1 | 8.8 |
|                                                 | 0.23  | 2.6  | 6.2  | < 0.01 | < 0.1 | 8.6 |
|                                                 | 0.24  | 2.7  | 6.1  | < 0.01 | < 0.1 | 8.7 |
| Hydroxide method (suspension of weak lime milk; technogenic waste) | 0.26  | 3.2  | 6.1  | < 0.01 | < 0.1 | 8.5 |
|                                                 | 0.23  | 3.1  | 6.3  | < 0.01 | < 0.1 | 8.8 |
|                                                 | 0.21  | 2.4  | 5.8  | < 0.01 | < 0.1 | 8.9 |
|                                                 | 0.22  | 2.8  | 5.8  | < 0.01 | < 0.1 | 8.8 |
|                                                 | 0.24  | 2.6  | 5.6  | < 0.01 | < 0.1 | 8.9 |
|                                                 | 0.26  | 2.7  | 5.7  | < 0.01 | < 0.1 | 8.8 |
|                                                 | 0.23  | 2.6  | 5.8  | < 0.01 | < 0.1 | 8.7 |
| Hydroxide method (suspension of brine treatment; technogenic waste) | 0.26  | 3.2  | 6.1  | < 0.01 | < 0.1 | 8.2 |
|                                                 | 0.23  | 3.1  | 6.3  | < 0.01 | < 0.1 | 8.4 |
|                                                 | 0.21  | 2.4  | 6.1  | < 0.01 | < 0.1 | 8.3 |
|                                                 | 0.21  | 2.8  | 6.3  | < 0.01 | < 0.1 | 8.4 |
|                                                 | 0.22  | 2.9  | 6.2  | < 0.01 | < 0.1 | 8.3 |
|                                                 | 0.24  | 2.5  | 6.3  | < 0.01 | < 0.1 | 8.4 |
|                                                 | 0.23  | 2.8  | 6.4  | < 0.01 | < 0.1 | 8.3 |

For the purification of process waters from manganese (II) and iron (III) ions, we propose technogenic waste: suspension of weak lime milk obtained after washing large quenching waste (large waste - incompletely burned material) and used for transporting small quenching waste (small waste) to the sludge collector channel, and slurry (suspension) of brine treatment sludge. This suspension mainly contains calcium carbonate and calcium and magnesium hydroxides.

Of interest is the use of slurry of brine treatment sludge (technogenic waste) to purify process waters in the lime kiln department from manganese (II) and iron (III) ions. All natural and artificial brines contain impurities in the form of Ca²⁺, Mg²⁺, SO₄²⁻ ions. At all soda plants, the brine is purified from these ions before entering production. For this, precipitation reagents are used, consisting of soda solution and diluted lime milk. When precipitating reagents are added to the brine containing sulfate and chloride salts of calcium and magnesium, reactions occur accompanied by the formation of calcium carbonate as well as calcium and magnesium hydroxides.[6]

The suspension formed after the precipitation of calcium and magnesium ions is separated into transparent brine and sludge in settling tanks. The clarified brine released from suspended particles is continuously removed from the upper part of the settling tank; the sludge is removed from the settling tank and pumped out into the waste.

The basis of the purification process of industrial waters from manganese (II) ions with suspension of weak lime milk is the neutralization of weakly acidic solutions. This process ends with self-regulating
formation of weakly alkaline medium, which excludes over-alkalization of solutions. The process itself consists of the precipitation of manganese (II) hydroxide during further oxidation to MnO(OH)$_2$ [3] and includes the absorption of Mn(II) ions by particles of the undissolved sorbent (calcium carbonate). In this case, the following reactions occur:

$$\text{Mn}^{2+} + 2\text{OH}^- = \text{Mn(OH)}_2\downarrow$$

$$\text{Mn(OH)}_2 + \text{O}_2 + \text{H}_2\text{O} = \text{Mn(OH)}_4\downarrow \rightarrow \text{MnO(OH)}_2\downarrow$$

Consideration of research results of various purification methods of process waters from manganese (II) ions made it possible to propose a local technological scheme for additional water purification using a suspension of weak lime milk as a reagent.

A schematic flow diagram of additional wastewater treatment is shown in figure 1.

**Figure 1.** Schematic diagram of wastewater treatment plant. T-1 - waste water tank; T-2 - tank for weak lime milk; MR-1 - mixer reactor; S-1 - settler; P-1-2-3 - pumps. Streams: I - industrial waste water; II - weak lime milk; III - treated waste water; IV - sludge.

Thus, a comprehensive study of the content of total and bivalent manganese compounds in limestone, water source, process and waste waters showed that the main source of wastewater pollution with manganese (II) ions is the raw material - limestone [7,8]. Along with increase in the depth of limestone mining along the horizons, an increase in bivalent manganese compounds is also observed.

A comparative study of various reagent methods for purifying process waters made it possible to develop a scheme for additional purification of manganese (II) ions by precipitation and coagulation with the suspension of brine purification sludge in the mixer reactor, followed by settling the sludge in sedimentation tanks. At the same time, the process water is purified from manganese (II) ions by at least 99.9%.

**References**

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