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TREATMENT OF WASTEWATER RESULTING FROM THE METALLIC COATINGS PROCESS

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ABSTRACT

The technological cleaning processes of steel strip surfaces used in metal coatings require organic or inorganic chemicals with a high risk of toxicity. To avoid pollution, the water resulting from these processes must be neutralized.

During the degreasing process, alkaline solutions containing caustic soda (NaOH), tri-sodium phosphate (Na_3PO_4) and detergents are used and the pickling process is made in 15-20% HCl solution. Rinse waters resulting from these operations will have an alkaline pH respectively acid pH, with values depending on the duration of use or refresh solution.

Neutralization was done with sulfuric acid solutions for alkaline water and sodium hydroxide solutions for acid water. The research aimed to establish the optimal conditions for neutralization and the optimal reagent consumptions.

KEYWORDS: cleaning surfaces, rinse waters, alkaline water, acid water, neutralization

1. Introduction

Treatment of wastewater generated by metallic coatings processes is essential prior to discharge of these wastewaters to wastewater collection systems or to the environment. Adequate treatment or pretreatment before discharge in wastewater collection systems is important to prevent toxic, corrosive, flammable or explosive wastes [1].

The wastewaters come from several different sources such as cleaning surfaces, preparation, production and rinsing processes, as well as the washing of equipment and production facilities [2, 3]. These processes produce various types of industrial wastes such as toxic organic solvents used as degreasing and cleansing agents, highly acidic or basic solutions used for the surfaces cleaning [4, 5].

Most of the hazardous wastewater comes from the rinsing operations applied after surfaces cleaning of the steel support. These waters may be highly acidic (low pH) or highly basic (high pH).

Different technologies exist for treatment of wastewater and effluents generated by the metal surface treatment industry. Treatment choice will depend on the composition of the effluents as well as the objectives and environmental needs of the company: zero liquid discharge, water reuse, adjustment of discharge limits, obtaining by-products, etc. [6].

Wastewaters with high pH levels are neutralized by the addition of acids such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). Also, carbon dioxide (CO_2) and sulfur dioxide (SO_2) can be applied in the gaseous form to decrease the pH of liquids [1].

Wastewaters with low pH levels are neutralized by oxides (CaO; MgO), hydroxides ($Ca(OH)_2$; $Mg(OH)_2$; NaOH) or soda ash (Na_2CO_3). Neutralization may be accomplished by either batch or continuous processes, depending on the amount of wastewater that will be treated [1].

The main methods of neutralizing these waters can be classified in three categories [7]:

- neutralization without water recirculation (open circuit) - applied before these waters are discharged to the sewer or in environment;
- with partial recirculation (semi-open circuit) - water treatment is done on the technological flow and recycled water is partially neutralized in the washing tanks. This method does not allow total reuse of the neutralized water because soluble ions (Na^+, Cl^-) remain in solution and, upon each reuse, their concentration increases;
- with total recirculation (closed circuit) - the neutralized water is completely recycled in the technological flow. The neutralization in closed

circuit is becoming more popular because it ensures a significant reduction in water consumption.

The research presented in this paper was aimed at neutralization of waters resulted from cleaning the steel strip surfaces in hot dip galvanizing processes. Were targeted the rinsing waters resulted after the degreasing and pickling processes.

In the process of alkaline degreasing of the steel strips surfaces for galvanizing, solutions which contain caustic soda (NaOH), trisodium phosphate (Na_3PO_4), detergents and other are usually used.

Pickling is made in acid solutions and the hydrochloric acid, 15-20% HCl solution is commonly used. In the technological flow, degreasing operations and pickling are followed by washing processes.

The wastewaters results will have an alkaline pH, respectively acid pH, with pH values depending on duration of use or refresh. These waters are treated for neutralizations up to a pH reaching 6.5-8.5 values, as required by normative (NTPA 002/2002).

2. Experimental researches

For the purpose of this research were intentionally prepared solutions with different pH values, respectively: acid solutions (with HCl): pH 2.64, 3.57, 4.30 and alkaline solutions (with NaOH) pH: 11.14; 12.27; 13.44.

2.1. Treating acidic waters

To treat acidic waters resulting from the washing process after pickling, the literature [8-10] indicates the use of a NaOH solution because it ensures simultaneous precipitation of metal ions through the following reaction:

$$Me^{2+} + 2NaOH \rightarrow Me(OH)_2 + 2Na^+$$

Work safety limits the concentration of caustic soda solution because it is a highly toxic and corrosive. Concentrated solutions can also affect the working installations.

For the treatment of acidic waters in the laboratory, there were introduced, while stirring and at room temperature, 5 mL 10% NaOH solution in 200 mL solution having an acid pH. After introducing the NaOH solution, we waited for 5 minutes for producing reactions and stabilizing pH.

It was recorded the resulting pH and the operation was repeated until the pH was neutral. Figure 1 presents the experimental results of the neutralization of the water with a pH of 2.64. It is observed that, for bringing the pH at value 6.83-7.50, which fits the normative, 25-30 mL NaOH solution was needed.

Figure 2 presents the experimental results of the water neutralization process with an initial pH of 3.57. It can be observed, similarly to the solution with pH 2.64, a rapid increase of the pH at introducing the first 5 mL NaOH solution and subsequently slower increase of pH values.

This evolution is explained by salt formation that has a buffering effect for the solutions that will be treated further.

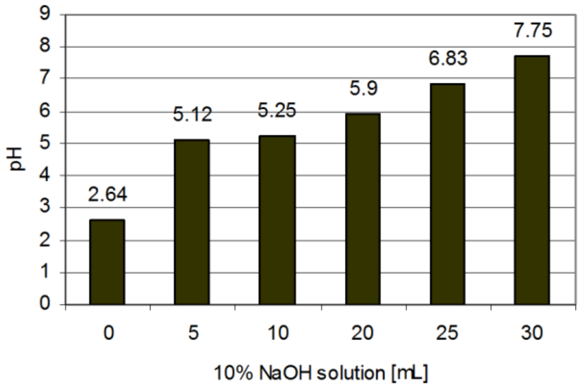

Fig. 1. *The variation of the pH for the solution with initial pH 2.64 depending on the amount of alkaline solution added*

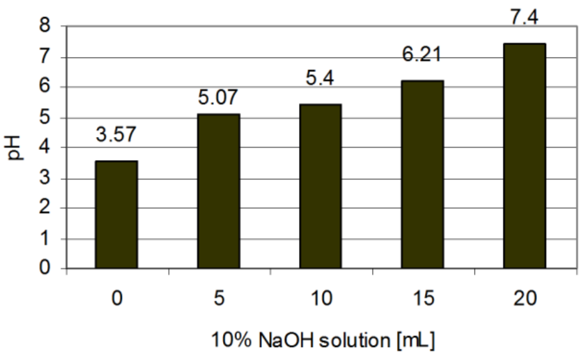

Fig. 2. *The variation of the pH for the solution with initial pH 3.57 depending on the amount of alkaline solution added*

As shown in Figure 3 if the initial pH is 4.30, neutralization occurs at the addition of 15 mL of NaOH solution.

The consumption of 10% NaOH solution to neutralize 100 L rinse water, with the different low values of pH is shown in Table 1.

Ii is observed that, to neutralize rinse water, with initial 2.5-3 pH, it is required a higher reagent consumption by 60% compared to the waters with pH value of 4-4.5. It is therefore indicated that the neutralization of the rinse water after pickling to be performed when they have a minimum pH value of 4.5. This reduces water consumption duration of the neutralization process, the amount of reagents and financial costs.

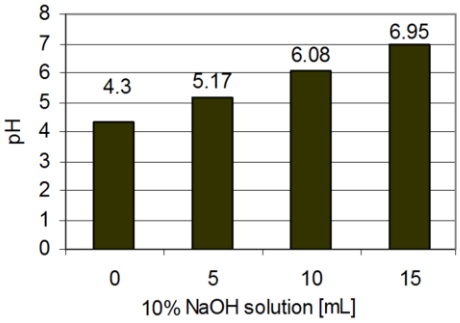

Fig. 3. *The variation of the pH for the solution with initial pH 4.30 depending on the amount of alkaline solution added*

Table 1. *Consumption of reagents required to neutralize the 100 L rinse water after pickling*

pH	2.5-3	3-3.5	4-4.5
10% NaOH solution [L]	12.5	10	7.5

2.2. Treating alkaline waters

To treat alkaline waters resulting from the washing process after degreasing, the literature indicates the use of an acid solution [10, 11]. For the treatment of alkaline waters in the laboratory we introduced, through stirring at ambient temperature, 2 mL of 25% H_2SO_4 solution in 200 mL solution having a basic pH determined. The results of the neutralization process are shown in Figures 4-6. In Figure 4 it is shown the neutralization results of the alkaline water with initial pH of 13.44. It is observed that, for bringing the pH at a value of 7.21, 10 mL of H_2SO_4 solution was needed.

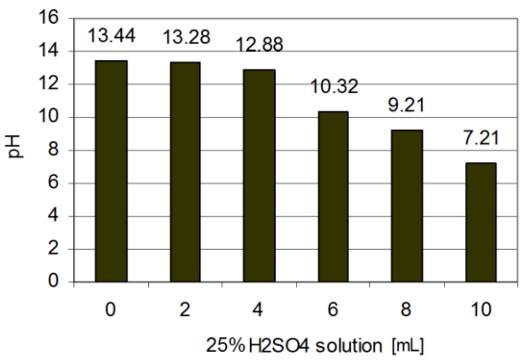

Fig. 4. *The variation of the pH for the solution with initial pH 13.44 depending on the amount of acid solution added*

Initial additions of the H_2SO_4 have a minor effect upon pH because the result product, Na_2SO_4 has little buffer capacity [6].

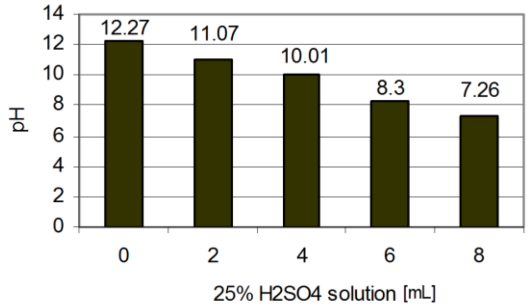

Fig. 5. *The variation of the pH for the solution with initial pH 12.27depending on the amount of acid solution added*

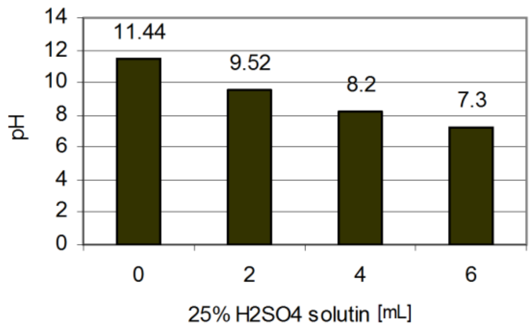

Fig. 6. *The variation of the pH for the solution with initial pH 11.44 depending on the amount of acid solution added*

The consumption of 25% H_2SO_4 solution to neutralize 100 L rinse water, with the different alkaline pH values, is shown in Table 2. The alkaline waters resulted after the rinse applied after degreasing are more easily neutralized for a pH minim 11 value.

Table 2. *Consumption of reagents required to neutralize the 100 L rinse water after degreasing*

pH	10-11.5	12-12.5	13-13.5
25% H_2SO_4 solution [L]	2	3	5

3. Conclusions

Neutralizing waters with acid pH, resulting following pickling process, should be made with less concentrated solution of caustic soda, because it favors the simultaneous precipitation of present metal ions. During neutralization with sodium hydroxide solutions, salts with buffering effect form quickly, stabilizing the pH.

Neutralizing alkaline waters, formed when rinsing following pickling process was performed with sulfuric acid solution of 25%. Following the process sodium sulfate will result, with reduced buffering effect.

Neutralization used for technological purpose or to avoid environmental pollution is performed up to a pH value of 6.5-8.5. Achieving these values through neutralization is done with lower reagents consumption and reduced process duration for acid waters with a maxim pH of 4.5, and for alkaline waters with a maxim pH of 11.

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