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Removal of Phosphorus in a Rinsing Process

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Abstract

This study deals with the removal of phosphates and phosphites along with other chelating agents from the electroless nickel bath, which creates environmental pollution by increasing the growth of algae and consequently eutrophication of natural water resources.

Key words : Phosphites, Hypophosphites, Lime, Hydrogen peroxide, Chelating agents.

With technological progress the natural environment has suffered from the increasing effects of pollution. The natural process of transportation of metal ions between the soil and water is affected and metal contamination occurs in high concentration that affects the natural ecosystem (1). It could cause permanent damage to ecological system (2). Emphasis has been laid on the removal of phosphites, phosphates or other organic chelating agents such as citric acid, tartaric acid, lactic acid and glycolic acid or EDTA which are used in electroless nickel. These organic acids and phosphates are presently found in the food chain and in sanitary sewage.

Analysis

Samples of water from two lakes and four sanitary sewages around two nickel plating units in Bangalore were tested it was found to contain very high concentration of phosphorus, which has its origin from the reducing agent hypophosphites ($NaHPO_2$) and decomposed products sodium phosphite (Na_2PO_2) (Table 1). In two of the electroless plating installation, the plant effluent from the electroless rinse water are raised in the pH 9 and 10 with lime water and then hydrogen peroxide is added to oxidize the PO_2 ion to PO_4 ion so as to convert it to the insoluble calcium phosphate.

Typically, electroless nickels are high in phosphorus content, which is traced to the reducing agents hypophosphites and the decomposition products of sodium phosphites. In two of the electroplating installations where limited phosphorus is used, the plant effluent from the electroless rinse water are raised in pH 10.0 with lime water and then hydrogenperoxide is added to oxidize the PO_2 ion to PO_4 ion so as to form the insoluble calcium phosphate.

Methods

The samples of spent electroless nickel which had 5–9 times turnover were treated with lime and hydrogen peroxide (Tables 1 and 2). The total PO_2 content and PO_4 content decreased from11.5 to 0.25g/liter. In this procedure, the PO_2 ion is oxidized by hydrogen peroxide to PO_4 ion where the excess lime reacts to reduce the phosphorus content. To reduce the phosphorus content to the minimum level, the PO_2 ion must be oxidized to PO_4 ion since calcium phosphate precipitates out.

Results and Discussion

It is reported that organic acids, such as citric acid, influence the removal of phosphorus (3—5). In

Table 1. Waste water source and conc of phosphorus.

Waste water source	Conc of phosphorus (mg/1)
Municipal sewage 1	5.0
Municipal sewage 2	6.5
Lake 1 (Naganathapura plant)	11.0
Lake 2 (Audogudi plant)	8.0
Lake 3 (Agrahara lake)	10.2
Lake 4 (Madiwala lake)	7.5

Table 2. Spent electroless nickel bath.

	Spent electroless nickel bath (g/liter)	Filtrate obtained after treatment with lime and H_2O_2 (g/liter)
Nickel	6.0	0.5
Hypophosphite	3.5	0.00
PO_4 ion	0.35	0.027
PO_2 ion	12.5	0.00
Total P as PO_4	11.5	0.025

Jar tests with raw sewage 3, it was found that presence of citrate reduced the ability of ferric chloride, alum, and lime to precipitate out phosphorus. It was found that if citrates were present the quantity of ferric chloride or alum required to achieve a given degree of phosphorus removal is higher. For example, studies indicated that the amount of alum required to achieve an effluent level of 1 mg/liter of phosphorus would increase by 67% in the presence of 10 mg/liter of citrate.However, when phosphorus removal was carried out during secondary treatment, no interference was noticed because the citrate easily degrades during secondary treatment.

Citrate degradation occurs in aerobic biological waste water treatment plants. It is known that citrate removal occurs in aerobic biological processes without the need for prior acclimations.

In view of the interference of the citric acid and other organic acids used as chelating agents in electroless nickel, the destruction of these organic acids were investigated. Potassium permanganate is used commercially to destroy EDTA in rinse waters from an electroless operation so that the effluent from the pretreatment could be utilized directly to hydroxide precipitation. The use of potassium permanganate to destroy other organic acids, such as maleic, succinic, hydroxyacetic and lactic acid and EDTA were investigated. All these organic acids to a greater or smaller extent react with $KMnO_4$. The end products formed are dependent on the reaction conditions such as $KMnO_4$concentrations, substrate concentrations, temperature, pH of reaction and presence of ions, such as Ca^{2+} or F^-, which may increase the reaction rate. Due to the complexity of the reactions, a single equation that accurately describes the reaction between $KMnO_4$and these organic acids cannot be written. However, to illustrate the several of the reactions taking place using citric acid, following reactions are shown (Fig. 1).

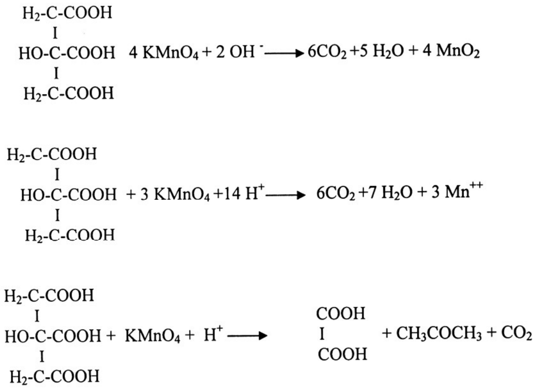

Figure 1. Reactions taking place using citric acid.

The reaction between permanganate and any of the organic acids will at best follow the last example bath and stop at the oxalic acid stage. One would need large amount of acid to get fast the oxalic acid stage. Under waste treatment conditions, $KMnO_4$will oxidize the hydroxy groups of the citric, lactic, and hydroxyacetic acids. For the other acids, maleic and succinic and EDTA, the $KMnO_4$ cleaves the double bond.

The oxidation and the decomposition of the chelating agents suggest a method for the complete waste treatment of electroless nickels. Such a method would be the decomposition of the chelates and subsequent addition of lime to precipitate out nickel as a hydroxide and phosphorus compounds as calcium phosphate.

Conclusion

This study has shown that it is possible to destroy the chelating agents in electroless nickel and at the same time reduce the phosphorus content in the electroless nickel effluent.

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