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PHYSICOCHEMICAL TREATMENT OF INDUSTRIAL WASTEWATER WITH THE MULTISTAGE NEUTRALIZATION PROCESS

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ABSTRACT

A complex industrial wastewater case is studied. The great variety of the products and the complexity of the production procedures render it impossible to apply a conventional technology for wastewater treatment. Initially an attempt was made to reduce the quantity and the organic load by reusing wastewater and by reclaiming useful substances or products from the wastewater. To further reduce COD the multistage neutralization process is studied by regulating the pH of the acid wastewater first in the alkaline region and then at pH 7. In this way COD removal is 18% greater than with the simple neutralization process at pH 7. Once this process was completed, since the effluent COD was not within the permissible limits, oxidation of the wastewater by using ozone was recommended. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Dyestuffs; industry; multistage neutralization; physicochemical treatment; wastewater.

INTRODUCTION

The plant we studied is located on the outskirts of Athens. Fifteen hundred tons of various dyestuffs (basic, disperse, direct and acid) plus five hundred tons of fluorescent brighteners are produced annually by a chain of complex processes in batch reactors. Over twenty products are produced. However only nine of these account for 95% of the total produced volume. For every product change a thorough cleaning of the installations is required. As a result the wastewater undergoes great changes in its chemical composition and behavior. The wastewater is of a high load in terms of COD, SS, TDS and the pH varies from acid to high alkaline values. Wastewater is produced during the following processes:

- tank cleaning,
- dewatering,
- drying,
- cooling water,
- steam production.

The aim of our project was to study the plant wastewater management so that the effluent could be safely discharged into the sewerage system of the city. At present the wastewater is discharged into the sewerage system after it has undergone neutralization with lime or sulfuric acid. For a period of forty days 4-hour composite samples were taken from the combined final effluent stream prior to neutralization. It was found that in 54% of the samples the pH level was below 6, in 34% above 9 and in only 12% was the pH level between 6 and 9, which are the limits defined by the municipal water company. COD follows a x^2 distribution with average value of 11,713 mg/l, median value of 7,000 mg/l and maximum value of 65,000 mg/l. At the same time the wastewater flow was monitored.

METHODS

The complexity of the production procedures and the great variety of products rendered it impossible to directly apply a conventional technology for wastewater treatment.

The first stage of our study involved reducing the quantity and the organic load of the various individual sources of pollution (reduction at source). The volume of the wastewater was reduced by: i) rescheduling of the production towards longer product runs and fewer product changes, i.e. fewer equipment cleanings taking into consideration the limited storage space of the company, ii) cleaning of the tanks and filterpresses by hot water under pressure instead of using tap water, and recycling of the wastewater to the production line, iii) recycling the steam traps water, the boiler relief water, the dionization columns water etc. As a result the wastewater flow was reduced from 600-650 m^3/d to about 320-440 m^3/d with average value 377 m^3/d (Poupaki *et al.*, 1992).

In order to reduce the organic load, reclamation of useful substances or products from the wastewater was considered. It was observed that most of the samples with high values of COD (more than 10,000 mg/l) contained quantities of various solvents. It was estimated theoretically that by reclaiming these solvents the average COD could be reduced from 11,713 mg/l to 7,161 mg/l, that is by 38.86%. Reclamation of these raw materials is justified in itself but it was the wastewater treatment which made the idea even more practical. It was estimated that the reclamation of dyestuffs which leak into the wastewater, comprising about 2% of the total quantity of dyestuffs, would result in only a slight decrease in effluent COD, 128 mg/l. Therefore it was not highly recommended. Finally it was estimated that the reuse of considerable quantities of wastewater would reduce the COD by at least 15%. As a result, the COD of the effluent stream after reclamation of raw materials and the reuse of wastewater was expected to be less than 6,000 mg/l.

To further reduce the organic load through the removal of the maximum possible percentage of dissolved organic substances a proper physicochemical method should be applied. For this reason the multistage neutralization process was studied. The method is based on the principle that every coagulant when used with a certain wastewater has its own optimum isoelectric point which is determined experimentally (Nemerow, 1978). The great variety of chemical substances in our case was suitable for testing the method. The method was optimized with the criterion being the maximum possible precipitation with the fewest stages of pH regulation. Sixteen of the 4-hour composite samples were treated. The selected samples represent those taken during the intervals of time when highest wastewater flows were registered. A controlled quantity of lime in powder form was added to the acid samples while a sulfuric acid solution of a specific normality was added to the alkaline samples for pH regulation. Furthermore, a 10 ml $FeSO_4$ solution 100% per weight as a coagulant was added to 1 liter of each sample and a rapid (flash) mixing followed. After the regulation of pH to the desirable level the solution was filtered, so that the next regulation would not cause redissolution of the precipitate. The precipitate was dryed and weighed. A sample was taken from the filtered solution for the measurement of COD and the rest of the sample was used for further treatment, i.e. new regulation of pH as is required for every experiment. The quantities of lime or sulfuric acid added to the solution and the produced quantity of the precipitate were also measured. All the experiments were repeated and the estimated COD removal, after every repetition of the method for the same sample, was within accepted limits. The use of filtration additives (polyelectrolytes) did not make any significant improvement.

Three multistage neutralization processes were compared:

- the gradual regulation of the initial pH at pH levels of 3, 5, 7, 9, 12 for the acid samples or at pH 9, 7, 5, 3 for the alkaline ones,
- the gradual regulation of the initial pH at pH levels of 7, 12 for the acid samples or at pH 7, 3 for the alkaline ones, and
- the direct regulation from the initial pH at pH 12 for the acid samples or at pH 3 for the alkaline ones.

In addition to the normal process, seven samples underwent filtration prior to pH regulation, because they contained significant quantities of suspended solids.

Finally there was an experimental neutralization of an acid sample with the use of packed bed limestone of 1-3 cm size which can achieve an effluent pH of about 5-6 (Patterson, 1985). The results are shown in Fig. 1.

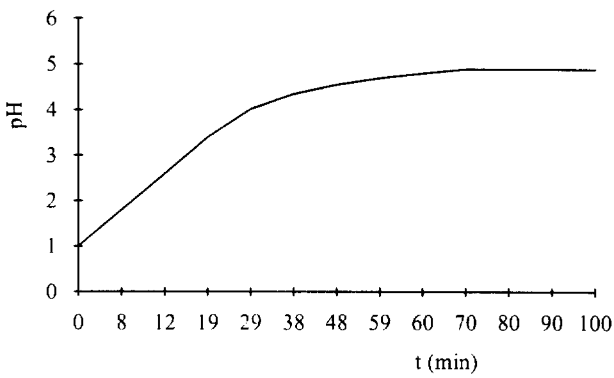

Figure 1. Neutralization of acid wastewater with limestone.

Table 1. Average removal of COD at various pH levels

pH	COD removal (%)
3	37.80
5	41.40
7	49.40
9	53.60
12	61.20
7	47.15
12	56.90
12	55.66

RESULTS AND DISCUSSION

The average removal of COD for the analyzed samples are shown in Table 1. From the results of the experiments the following can be concluded:

a) The reduction of COD of the acid samples increases monotonically with the gradual regulation of pH but there is no significant differentiation in the reduction compared with that of the direct regulation method either to 7 or to 12.

b) The initial filtration does not affect the removal of COD. The SS of the sample are removed during the first settling and they do not have acidity which consumes alkali.

c) The neutralization with lime or sulfuric acid and the simultaneous addition of ferrous sulfate result in significant reduction of COD in two thirds of the samples.

d) The average COD reduction for the acid samples is 47.15% at pH 7 and 55.16% at pH 12, i.e. 18% greater than the reduction at pH 7.

e) The gradual regulation of pH at 12 compared with the direct regulation at 12 shows a slight and therefore insignificant increase in COD removal in only a few samples.

f) The regulation of pH of the alkaline samples first in the acid range and then at 7 does not significantly influence the reduction of COD.

g) The separation of precipitates by filtration or by 2 hours settling does not have an impact on the reduction level of COD.

With the application of the above mentioned process the final value of effluent COD is 1632 mg/l. The permissible limit for the disposal in the sewerage system of the city is 1000 mg/l. To further reduce COD the method of chemical oxidation with ozone was recommended (Liakou and Lyberatos, 1995). This method will reduce COD by at least 40% (if the effluent contains only dyes) but generally by more than 50%, while the use of ozone achieves significant decolorization of the effluent as well.

Furthermore, the possibility of continuing with biological treatment, after physicochemical treatment was complete, was considered. A pilot plant was set up for this purpose and received a supply of neutralized waste for a period of at least four months. Despite repeated injections of microorganisms extracted from an operating domestic sewage treatment plant no sludge resulted. This failure was attributed to the fact that there were great variations of wastewater versus time regarding flowrate, chemical composition and organic load which do not allow acclimatization and the development of microorganisms. The problem is so acute that it cannot be overcome by providing a reasonable size equalization tank.

In the light of these conclusions the suggested physicochemical treatment for the acid wastewater includes the following stages:

- Neutralization with limestone filterbeds.
- Regulation of pH at 12 with simultaneous addition of coagulant.
- At least two hours settling.
- Regulation of pH at 7.
- At least two hours settling.
- Ozonation.
- Return of sludge in flash mixing tank for the improvement of the coagulation and use of the alkali of sludge.
- Return of sludge in limestone bed tank for use of its alkali and reduction of the produced sludge.

For the alkaline wastewater the suggested treatment is the same except for the neutralization with limestone and the addition of lime at pH 12. Sulfuric acid is used for pH regulation at 7 instead.

CONCLUSIONS

The multistage neutralization process was considered for a complex case of industrial wastewater. This method is recommended because of the great variety of chemical substances used in this plant. It includes the regulation of pH level of the wastewater at different pH levels. In our case it was proved that regulation of pH level of the acid wastewater first at twelve and then at seven with an intermediate 2 hours settling achieves significant removal of COD.

By applying this process, in combination with the reclamation of raw materials, the reuse of wastewater and the oxidation by ozone, we can obtain characteristics of the treated wastewater which are within the permissible limits.

Finally there is minimal use of $Ca(OH)_2$ by neutralization of acid wastewater with limestone.

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