



# A CONVENIENT COST-EFFECTIVE METHOD FOR RECYCLIZATION OF THE AQUEOUS WASTE EFFLUENTS OF CAR-PAINTING INDUSTRY

**László Kótai,<sup>\*[a,b]</sup> Tünde Kocsis,<sup>[a]</sup> Anna Jánosity,<sup>[a]</sup> Imre Kovács,<sup>[c]</sup> Kalyan K. Banerji<sup>[d]</sup> and Anna Mária Keszler<sup>[a]</sup>**

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Non-sedimentation nanoparticles containing alkaline wastewater as effluent from the cleaning process of car-painting lines can be purified by sedimentation after adding of mineral acids to adjust the pH below 5. Using 10 % aq. sulfuric acid to coagulate and filtrate the colloid particles, and adjusting the effluent pH with 10 wt. % aq. NaOH to the original value (~9), the wastewater can be recycled with ca. 0.3 % salt content into the cleaning process of the painting line (rinsing) technology.

\* Corresponding Authors

E-Mail: kotai.laszlo@ttk.mta.hu

- [a] Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar Tudósok krt. 2., Budapest, H-1117, Hungary.
- [b] Deuton-X Ltd., H-2030, Érd, Selmeci u. 89.
- [c] NÓGRÁD Chemical Works, Tolmács, Arany J. u. 2.
- [d] J.N.V. University, Jodhpur 342005, Rajasthan, India.

## Introduction

During the paint processes in car plants, the paint to be applied to the car bodies are changed frequently. To avoid intermixing of different colors the application systems has to be cleaned before every change by means of a rinsing liquid.<sup>1</sup> These rinsing waters are recycled based on an evaporation or a fractionated condensation process with the treatment of the condensates.<sup>2</sup> The energy demand of evaporation, however, initiated finding new possibilities, like the oxidation processes, for example with ozone, ozone combined with hydrogen peroxide, photo-Fenton treatment, and coagulation-flocculation methods as well.<sup>3</sup> The aqueous rinsing liquids, however, contains not only the pigment particles but some organic components like butyl glycol or tensides as well, thus oxidation processes destroy these components. The bacterial treatment of these type of wastewaters is time consuming and further treatments are needed to recycle the purified water into the technological processes.<sup>4</sup>

The aim of the present study was the development of a simple and cost-effective method to remove the suspended solids and recycling the cleaning liquid into the car-painting plant with coagulation technique without using oxidants, bacteria, and high-cost evaporation processes.

## Experimental

The wastewaters (two samples were taken at the same time in every day for 6 days (6x2 black sample (1a,b-6a,b) and 4x1 purple samples (7-10)) were taken from an

operational car-painting line washing liquor. The samples were stored for 2 weeks without the appearance of any sedimentation. The neutralization was done with 1 M HCl or H<sub>2</sub>SO<sub>4</sub> and 1.5 M HNO<sub>3</sub> solutions. In the experiments performed with H<sub>2</sub>SO<sub>4</sub> (1M, ~10 %), a sample was selected which had the highest acid consumption and the amount of sulfuric acid (1.50 % toward the wastewater sample) required to reach the pH 4 was determined. This amount of 10 % aq. sulfuric acid was used to acidify the all other further samples. The acidified samples were filtered with filter paper, the filter cake was dried and weighted, then the filtrate was treated with 10 % aq. NaOH to control the pH to near the starting value. The adjustment of pH was done with using standard pH meter.

All the chemicals used were supplied by Deuton-X Ltd, Hungary. X-ray powder diffractograms were recorded using a Philips PW-1050 Bragg-Brentano parafocusing goniometer. It was equipped with a Cu tube (40 kV and 35 mA), a secondary beam graphite monochromator and a proportional counter. Scans were recorded in step mode. The diffraction patterns were evaluated by full profile fitting techniques.

## Results and Discussions

The starting pH values of the samples were varied between 8.86 and 9.37 and there was no observed sedimentation in a week. The stable colloid state is supposed to be due to hydroxide ion adsorption and repulsion of negatively charged nanoparticles. According to this, compensation of negative charges was expected to initiate aggregation and sedimentation by adding different mineral acids. The results can be seen in Table 1.

As it can be seen from Table 1, the nitric acid cannot decrease the pH to the level available with HCl or H<sub>2</sub>SO<sub>4</sub> due to its oxidative nature and consumption of the acid for oxidation of some organic contaminant. therefore, using nitric acid is not suggested. Since the HCl and H<sub>2</sub>SO<sub>4</sub> solutions gave almost the same results, and because the sulfuric acid is much cheaper than aq. HCl, only the sulfuric acid was used in the further experiments.

**Table 1.** Effects of mineral acids on car painting wastewater sedimentation ability

| Wastewater (200 mL),<br>initial pH=8.65        | 1 M HCl  | 1.5 M HNO | 1.5 M HNO <sub>3</sub> | 1 M H <sub>2</sub> SO <sub>4</sub> | 1 M H <sub>2</sub> SO <sub>4</sub> |
|--|----------|-----------|------------------------|------------------------------------|------------------------------------|
|  | Sample 1 | Sample 1  | Sample 2               | Sample 1                           | Sample 2                           |
| Added acid amount                              | 4.6 mL   | 3.0 mL    | 2.9 mL                 | 2.8 mL                             | 2.9 mL                             |
| pH after acid addition                         | 4.6      | 4.6       | 5.25                   | 4.6                                | 4.2                                |
| Amount of dry precipitate, g                   | 2.56     | 2.55      | 2.52                   | 2.56                               | 2.53                               |
| Filtrate, pH                                   | 5.0      | 6.0       | 5.5                    | 6.0                                | 5.2                                |
| NaOH added, 10% (wt.), in mL to reach pH =8.63 | 1.2      | 1.1       | 1.2                    | 1.0                                | 1.0                                |

**Table 2.** Results of sulfuric acid precipitation and re-alkalization of the car-painting plant aqueous effluents.

| Sample | Initial pH    |                     |                     | Dry material. % (wt.) | V <sub>NaOH</sub> /V <sub>H<sub>2</sub>SO<sub>4</sub></sub> |
|--------|---------------|---------------------|---------------------|-----------------------|---|
|        | Initial value | After acid addition | After NaOH addition |                       |   |
| 1a     | 8.86          | 3.88                | 8.89                | 0.85                  | 1.00  |
| 1b     | 9.08          | 3.81                | 9.17                | 0.85                  | 1.07  |
| 2a     | 9.01          | 4.01                | 8.98                | 0.86                  | 1.00  |
| 2b     | 9.04          | 3.91                | 8.92                | 0.85                  | 1.00  |
| 3a     | 9.37          | 2.23                | 9.25                | 0.33                  | 1.13  |
| 3b     | 9.37          | 2.24                | 9.20                | 0.33                  | 1.07  |
| 4a     | 9.36          | 2.23                | 9.36                | 0.33                  | 1.13  |
| 4b     | 9.33          | 2.30                | 9.38                | 0.33                  | 0.97  |
| 5a     | 9.36          | 2.29                | 9.44                | 0.33                  | 1.13  |
| 5b     | 9.35          | 2.26                | 9.22                | 0.33                  | 1.10  |
| 6a     | 9.07          | 4.13                | 9.07                | 0.84                  | 0.97  |
| 6b     | 9.09          | 4.02                | 9.11                | 0.83                  | 1.00  |
| 7      | 8.90          | 2.76                | 9.09                | 0.78                  | 1.13  |
| 8      | 9.04          | 3.70                | 9.07                | 0.86                  | 1.00  |
| 9      | 9.26          | 3.55                | 9.06                | 0.98                  | 1.00  |
| 10     | 9.26          | 3.90                | 9.21                | 0.98                  | 1.00  |

Use of 10 % aq. sulfuric acid to neutralize the surface-bound hydroxide ions with the hydroxonium ions, resulted in a fast aggregation, and sedimentation of the particles was observed below pH 5. Depending on the composition of the wastewaters, the same amount of sulfuric acid resulted in different pH values, therefore 1.5 % amount of a 10 % (wt.) sulfuric acid was used in every case, and the pH values found after acid addition can be seen in Table 2.

The aggregated solids could easily be filtered in every case. The amount of the wet filter cake and the dry solid residue are also given in Table 2.

The reaction mixtures were filtered and the filter cake was dried in air at room temperature, then the filtrate was treated with 10 % aq. NaOH to adjust the pH near the initial pH value of the wastewater. Comparing the ratio of 10 % aq. NaOH volume toward the previously used 10 % aq. H<sub>2</sub>SO<sub>4</sub> volume clearly shows that this value was varied between 0.97 and 1.13, thus the salt amount forms in the system is below 0.3 %. This low salt content permits to recycle the treated and alkalinized cleaning liquid into the original technology.

Two cubic meters of wastewater was treated with 1.5 % amount of 10 % aq. sulfuric acid, then after filtering and alkalinizing with 1.5 % aq. NaOH, the operating painting line could use that in a usual way without appearance of any adverse effect.

The solid residues removed by filtration were proved to be X-ray amorphous, but their heat treatment at 500 and 1000 °C led to the crystalline calcite (CaCO<sub>3</sub>) and wollastonite (CaSiO<sub>3</sub>), respectively. (Heat treatment was used to compact the volume/amount of solid residue). Some amount of amorphous materials was also detected in both heat-treated samples (Supplementary Figures 1 and 2). The reason for the difference in the phases observed at 500 and 1000 °C is that the amorphous SiO<sub>2</sub> particles can react above 500 °C with CaCO<sub>3</sub> and results in the formation of CaSiO<sub>3</sub>. A small amount of TiO<sub>2</sub> was also found, but TiO<sub>2</sub> can react in an analogous way with CaCO<sub>3</sub> as the SiO<sub>2</sub> but with the formation of CaTiO<sub>3</sub>.

In order to eliminate/diminish salt-formation and accumulation of these salts in the purified cleaning liquid, a solid tertiary-amine based ion-exchange (solid base) technology has just been studied and tested to neutralize the sulfuric acid content of the cleaning liquid.

## Conclusion

Nanoparticles containing alkaline wastewater from the car-painting factories can be purified with an addition of 10 % aq. sulfuric acid to coagulate the colloid particles, and the effluent can also be recycled with ca. 0.3 % salt content into the cleaning process after filtration of the solid sediments and adjusting the pH with the same amount of 10 % aq. NaOH as the amount of sulfuric acid solution was used.

## References

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