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MONITORING OF PORCELAIN INDUSTRY WASTEWATER CASE STUDY: SC APULUM SA ALBA IULIA

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Abstract

The paper aimed to assess the quality of wastewater resulted from the water treatment plant of a porcelain factory from Alba Iulia. Two of our society's biggest problems are water pollution and wasteful use of freshwater. Although industry is not the main user of water resources, it is the main responsible for water pollution. Monitoring of porcelain industry wastewater provided the information needed for the identification of water pollution problems. The following water quality indicators have been analyzed: pH, suspended solids, fixed residue, chemical oxygen demand (the dichromate method), calcium and aluminum. During the year 2012, the values of the analyzed indicators didn't exceed the maximum admitted limits established by NTPA 001, except by suspended solids, which recorded higher values for all analyzed samples. In conclusion, the monitoring of the porcelain industry wastewater revealed the fact that the main pollutant generated by this economic activity is represented by suspended solids, whose removal requires additional water treatment methods.

Key words*: monitoring, porcelain industry, suspended solids, wastewater.*

INTRODUCTION

Water is essential for life and it is indispensable for agriculture and industry (Bartram and Helmer, 1996). However, freshwater is a finite resource: although over 70% of the Earth's surface is covered by water, less than 1% of all water resources are available for human consumption; the other 99% of water resources are represented either by saltwater (oceans), and hence they are too salty to be used for most purposes, or by frozen freshwater (ice caps and glaciers) (Banu and Radovici, 2007).
FAO Aquastat revealed the fact that the demand for freshwater is continuously increasing, the main users of water resources being represented by: agriculture (59%), domestic sector (23%) and industry (18%). Although human use of water for almost all purposes results in the deterioration of water quality, the most important source of water pollutants (in the range of thousands of different chemical substances) remains industry (Meybeck et. al, 1996; Petre and Teodorescu, 2009). Because of that, monitoring of industrial wastewater has become a necessity for all factories that use water resources.

As far as ceramic industry is concerned, a previous study conducted by Dincer and Karg (2000) reported the following characteristics of the wastewater resulted from this economic activity: high concentrations of suspended and dissolved solids, significant COD level and low concentrations of heavy metals (lead, cadmium, iron, copper and manganese). However, the porcelain industry wastewater may have different characteristics, depending on the technological process and the chemical substances that are used.
According to Reference Document on Best Available Techniques in the Ceramic Manufacturing Industry (CER BREF, 2007), the wastewater resulted from the manufacturing of household ceramics arises from the cleaning of the installations and from the glazing and decorating processes and it contains the same components as the raw materials.
At the Apulum porcelain factory from Alba Iulia the following raw materials are used:

- kaolin ($Al_2Si_2O_5(OH)_4$), feldspar (silicates of aluminum, containing

sodium or/and potassium) and quartz (SiO_2): for the porcelain body and for the glaze;
- plaster (results from the calcination of gypsum, $CaSO_4 \cdot 2H_2O$): for the ceramic moulds;
- ceramic pigments: used in smaller quantities, in the decorating process.

Hence, besides suspended solids and organic substances, industrial wastewater resulted from this porcelain factory may contain also aluminum and calcium ions.

Before being discharged to the city's sewer system, industrial wastewater passes through the wastewater treatment plant of the Apulum factory and a part of the suspended solids are removed through gravity settling in a double-compartmented sedimentation tank. As the municipal treatment plant is under construction, the sewer system conveys the water directly into the Mureş River and therefore wastewater monitoring is indispensable in order to control pollution.

MATERIALS AND METHODS

In order to monitor the wastewater released from the wastewater treatment plant of the Apulum porcelain factory, the following water quality indicators have been analyzed: pH, suspended solids, fixed residue, chemical oxygen demand (the dichromate method), calcium and aluminum. Determination of these six indicators was realized during the year 2012 and it was based on the standard methods presented in Table 1:

Table 1. The methods used for the determination of the water quality indicators

Nr.	Indicator	Standard
1.	pH	SR ISO 10523/1997
2.	Suspended solids	STAS 6953/1981
3.	Fixed residue	STAS 9187/1984
4.	COD (Cr)	SR ISO 6060/1996
5.	Ca^{2+}	STAS 3662/1990
6.	Al^{3+}	STAS 9411/1983

- for the determination of pH it was used a pH-meter;
- suspended solids were determined by passing the samples through a filter. This filter was weighed before and after filtration and drying. The increase in filter weight represents the total suspended matter;
- fixed residue was determined by evaporating the water from the sample and weighing the remained residue after it has been dried;
- COD's determination was based on the oxidation of the organic matter from the samples by potassium dichromate, in acid environment and in the presence of a catalyst. Oxidation takes place when this mixture is boiled under reflux. COD was calculated after the titration of the remained dichromate with ferrous ammonium sulphate;
- Ca^{2+} was determined by the titration of the sample with EDTA solution, in the presence of murexide indicator, until the water color changed from red to violet (this change in color appeared when all of the calcium ions have been complexed by EDTA). The concentration of calcium ions was calculated from the volume of EDTA used for titration;
- Al^{3+} was determined using the colorimetric method: in a limited range of pH, aluminon reacts with aluminum ions from the sample and the water color changes in red. The absorption of this red solution is proportional with the concentration of Al^{3+}. In order to calculate the concentration of the aluminum ions, the absorption of the red mixture was measured using a spectrophotometer.

Water samples were collected from three points, as it follows:
- all six indicators were determined at the release of the wastewater from the sedimentation basin, in order to assess compliance with regulatory requirements and to identify existing pollution problems.
- at the entrance of the wastewater into the sedimentation tank were determined chemical oxygen demand and suspended solids, in order to calculate removal efficiency for these two indicators.

- for the analysis of the suspended solids, samples were taken also from the discharging pipe; thus, it was taken in consideration the possible change in concentration of suspended solids due to the interaction between water and pipes.

The six water quality indicators were analyzed from three in three months (in March, June, September and December), except by suspended solids, fixed residue and pH, whose monitoring included also monthly analyses between June and September.

Experimental results obtained during the year 2012 are presented in the Table 2.
SB – Sedimentation basin
DP – Discharging pipe
LOD – Detection limit (6 mg/l)
NTPA 001 – Regulations on wastewater discharge conditions in rivers
NTPA 002 - Regulations on wastewater discharge conditions in the sewer system
MAV, MAC – Maximum admitted value (concentration)
MinAV - Minimum admitted value
MaxAV – Maximum admitted value

RESULTS AND DISCUSSIONS

Table 2. Experimental results obtained during the year 2012

Indicator			Month						NTPA 002	NTPA 001	Maximum admitted value (MAV/ MAC)*
			Mar	Jun	Jul	Aug	Sep	Dec			
Suspended solids (mg/l)	SB	Inlet	1123	894	989	1123	698	1211	-	-	-
		Outlet	122	93	98	106	61	123	-	-	-
	DP		127	117	114	131	79	132	350	35	130
Fixed residue (mg/l)			979	898	896	950	611	882	-	2000	2000
pH			7,5	7,5	7,5	7,5	7,5	8,0	6,5 - 8,5	6,5 - 8,5	6,5 -8,5
Al^{3+} (mg/l)			0,58	0,62			0,70	0,70	-	5	5
Ca^{2+} (mg/l)			148,66	146,62			148,2	162,33	-	300	300
COD (mg/l)	Inlet		22,6	14,9			23,5	30,2	-	-	-
	Outlet		<LOD	12,0			13,9	11,0	500	125	125

*As the sewer system doesn’t convey the water in a municipal wastewater treatment plant, but in the Mureş River, the competent authority established specific discharging conditions, according to regulation in force.

Therefore, the admitted effluent value for suspended solids (130 mg/l) is smaller than the value given in NTPA 002 (350 mg/l), but higher than the value given in NTPA 001 (35 mg/l), while for the other five monitored indicators the maximum admitted values are those given in NTPA 001.

The concentration of suspended solids slightly exceeded the maximum admitted value established by the competent authority (130 mg/l) in two of the analyzed months: in August, the recorded value was 0,77% higher than the maximum admitted value and in December it was 1,54% higher than this limit (Figure 1).

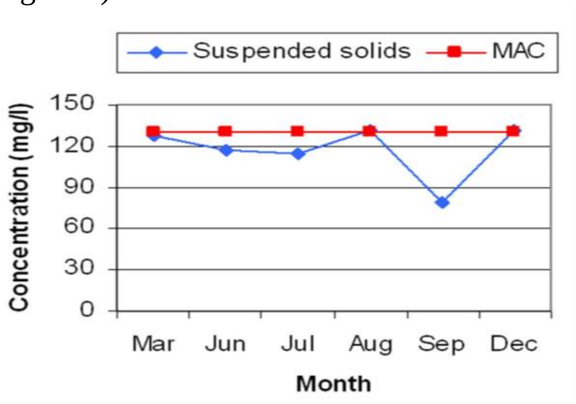

Figure 1. Comparison between the concentrations of suspended solids and the maximum admitted concentration (MAC) established by the competent authority

Compared to the maximum admitted value from NTPA 001 (35 mg/l), all values registered for the suspended solids were much bigger than the limit: the lowest measured concentration was 2,25 times bigger than this limit, while the highest was 3,77 times bigger (Figure 2). This is the reason why, even though the other indicators were monitored only from three in three months, suspended solids and fixed residue were monitored monthly between June and September.

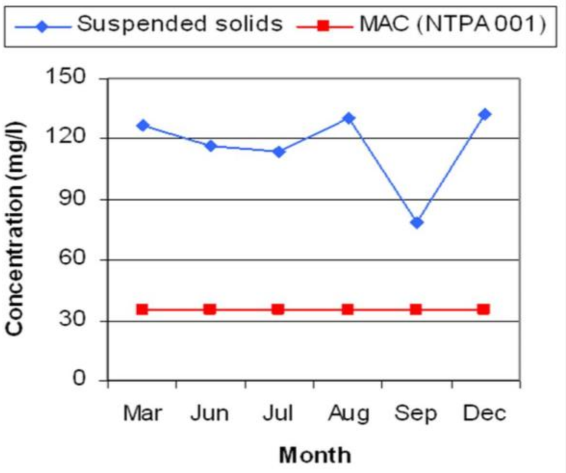

Figure 2. Comparison between the concentrations of suspended solids and the maximum admitted concentration (MAC) given in NTPA 001

Even though suspended solids pose no risk to human health, when their concentration in wastewater is high they can cause many environmental problems. As they are neither dissolved, nor settled in the water, suspended solids may increase water turbidity, triggering a "domino effect": on one hand, the amount of light that passes through the water is reduced, and hence photosynthesis slows down and some of water vegetation may die. As the photosynthesis decreases and dead vegetation is decomposed, less oxygen is produced in water while more oxygen is consumed by bacteria and this leads to a decrease in the amount of dissolved oxygen. Further, low dissolved oxygen is responsible for an increase in fish mortality. On the other hand, suspended solids absorb heat from sunlight and hence water temperature increases, resulting in an even lower level of dissolved oxygen in water (http://water.me.vccs.edu/courses/ENV211/lesson20.htm).

The values obtained for fixed residue didn't exceed the maximum admitted value: for all analyzed samples, the measured concentration was smaller than half of the limit (Figure 3). These results show the fact that the analyzed wastewater contains low concentrations of dissolved substances.

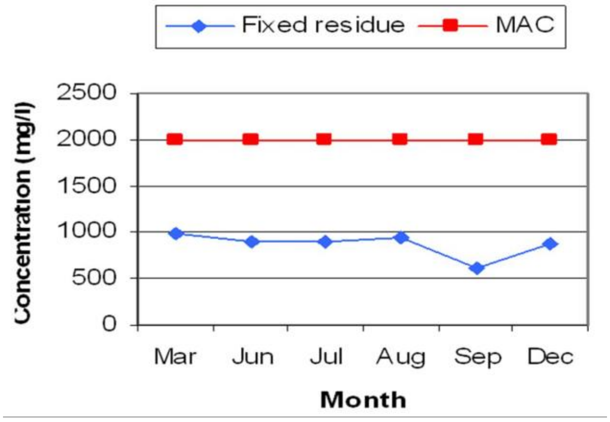

Figure 3. Variation of fixed residue

The pH had a constant value for all samples, except the last one, which had a higher value than the other five. Anyway, all measured values were situated in the admitted range of pH (Figure 4).

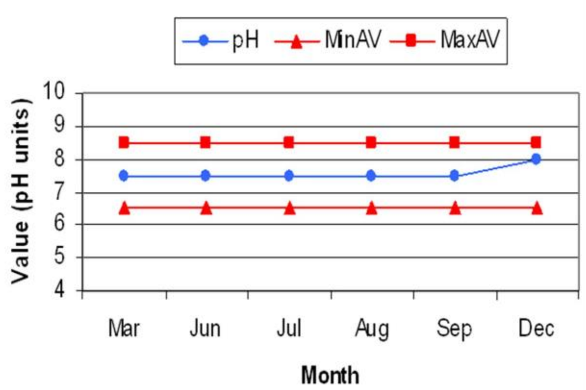

Figure 4. Variation of pH during the year 2012

The concentrations of aluminum and calcium were situated under the maximum admitted values. For calcium, the maximum admitted concentration was 2 times higher than the measured concentration, while for aluminum the maximum admitted concentration was 7-8 times higher than the measured concentration (Figure 5, 6).

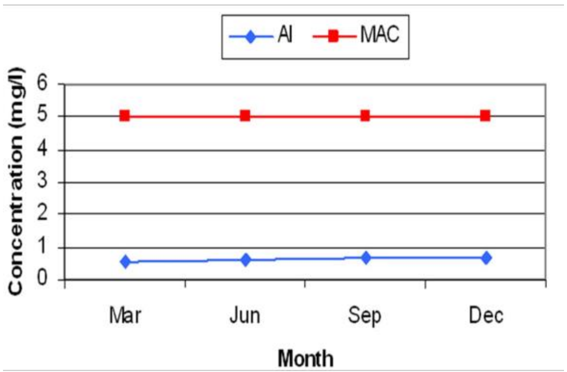

Figure 5. Variation of aluminum concentration during the year 2012

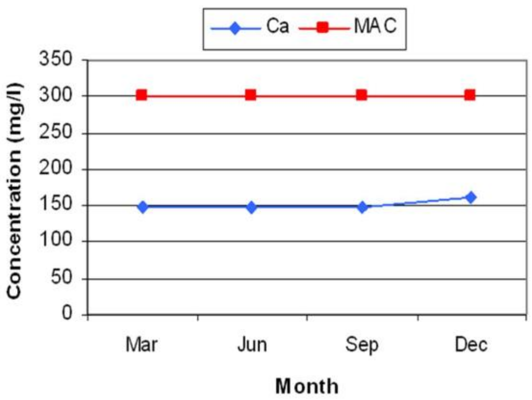

Figure 6. Variation of calcium concentration during the year 2012

Unlike the observations made previously by Dincer and Karg (2000) in a study concerning ceramic industry wastewater, for the analyzed porcelain factory, COD level is not a problem. On the contrary, for COD the maximum admitted value is more than 10 times higher than the measured value (Figure 7). Consequently, the wastewater resulted from Apulum has a low content of organic substances.

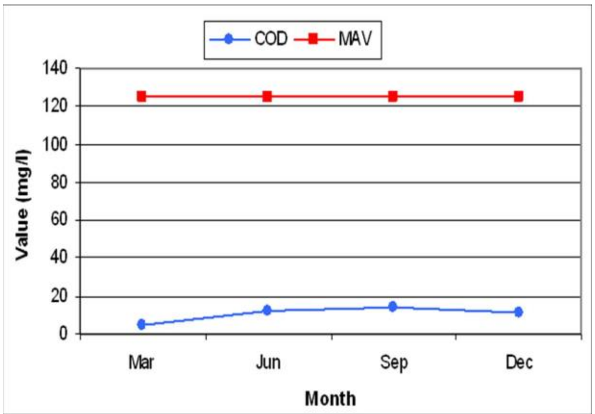

Figure 7. COD variation during the year 2012

By analyzing the concentrations of suspended solids and COD both at the wastewater treatment plant inlet and outlet, it was possible to calculate the removal efficiency for these two pollutants, applying the following formula:

$$\beta = \frac{M - m}{M} \cdot 100,$$

where: β – degree of purification (removal efficiency)

M – initial concentration of the pollutant for which the purification degree is calculated (mg/l)

m – concentration of the same pollutant after treatment (mg/l)

For the removal of organic substances (COD), the average efficiency was 50,44%. However, the degree of purification was good in most of the analyzed months (up to 77,9%) and only in a single month it was registered a low value (19,5%) (Figure 8).

As suspended solids are concerned, the average removal efficiency was 89,96% and there were no significant oscillations in monthly values: the maximum registered value was 91,3%, while the minimum was 89,14% (Figure 8). The purification degree is high, but the initial concentration of suspended solids is also high (the average concentration during the year 2012 was 1006 mg/l), and because of this additional water treatment is required.

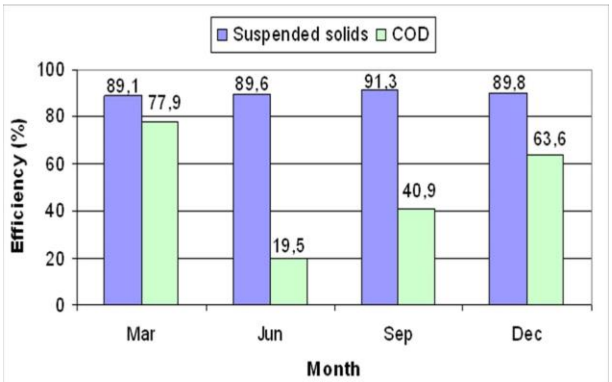

Figure 8. Removal efficiency for suspended solids and COD

To enhance the removal of suspended solids, Reference Document on Best Available Techniques in the Ceramic Manufacturing Industry (CER BREF, 2007) recommends using flocculation and coagulation agents, such as alums or polyelectrolyte and/or a combination of lime and metal salts.

However, conventional inorganic coagulants have risen environmental and health concerns because of the residual aluminum that may be present in water and sludge after the treatment with alum or poly aluminum chloride. A more eco-friendly coagulant and flocculant is chitosan, a biodegradable compound. This biopolymer is considered to be even more effective than alum for removal of kaolinite suspensions and it produces less, non-toxic sludge (Divakaran and Pillai, 2001; Chatterjee et al, 2009).

CONCLUSIONS

Monitoring of wastewater resulted from Apulum factory highlighted the fact that the main pollutants generated by porcelain industry are suspended solids (most of them inorganic solids), whose concentrations exceeded the maximum admitted value given in NTPA 001 for all analyzed samples. However, the porcelain factory complies with regulatory requirements, as the maximum discharging limits approved by competent authorities are higher than the maximum admitted limits given in NTPA 001.

The values of the other monitored indicators (fixed residue, chemical oxygen demand, pH, calcium and aluminum) were situated under the admitted limits.

At present, the method used at the analyzed porcelain factory for the removal of suspended solids is sedimentation. Even though this treatment method registered a removal efficiency of up to 91,3%, wastewater enters the treatment plant with a significant concentration of suspended solids (up to 1123 mg/l) and hence additional water treatment is required in order to prevent water pollution.

The settleability of suspended solids may be increased by combining sedimentation and coagulation processes. According to recent research on suspended solids removal, one of the most effective coagulants is chitosan, which, unlike conventional coagulants, produces no secondary effects.

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