Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28249

250 (2022) 100–107
February

Treatment of a nano-ceramic coating bearing effluent integrating adsorption and a coagulation/flocculation process

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Received 22 September 2021; Accepted 21 January 2022

ABSTRACT

In the metal mechanics industry, the surface treatment by nano-ceramic coating results in the generation of a hard-to-treat industrial effluent. The treatment process by coagulation/flocculation/sedimentation usually presents non-conformities regarding the emission standard in terms of organic load. The objective of this work was to improve the removal of chemical oxygen demand (COD) with the use of powdered activated carbon (PAC) prior to the coagulation/flocculation process. The procedure applied consisted of dispersion of the PAC particles in the raw effluent for adsorption of soluble contaminants, followed by hetero-aggregation of PAC and the suspended pollutants with the use of polyaluminum chloride and polyacrylamide. The addition of PAC, at a concentration of 0.5 g L^{-1}, resulted in a reduction of more than 50% in the residual concentration of organic load compared to the conventional treatment. The integration of adsorption with the coagulation/flocculation process met all effluent emission conditions established by the environmental agency, as well as significant gains in reducing toxicity. This technique ensured greater operational stability in the removal of COD observed through statistical capability analysis (Cp). The addition of PAC to the process increased the weight amount of sludge, but this was not an impediment in operational and cost terms.

Keywords: Nanoceramics; Effluent treatment; Coagulation/flocculation; Adsorption; Powdered activated carbon; Air conditioning production

1. Introduction

The global air conditioning systems market size was USD 106.6 billion in 2020 and it is expected to register a compound annual growth rate of 6.2% from 2021 to 2028 [1]. Each air conditioner system is assembled in a steel structure that receives conversion coating, called surface treatment, with anticorrosive and preparatory purposes for the application of powder paint. The conversion coating is an inorganic layer formed on the surface of a metal from the immersion or sprinkling of an aqueous solution containing the required ions to precipitate on the surface. Surface coating processes of steel include galvanisation, chromatisation, phosphatisation and nanoceramics [2].

In the case of nano-ceramic coatings, the process originated at the beginning of the 21st century with the use of acid solutions of hexafluorozirconium, proved to be less harmful to the environment [3]. Currently, nano-ceramic coatings are obtained by immersion of metal parts in solutions containing titanium and zirconium ions, among others, and are generically so-called due to their inorganic nature and thickness of the order of tens of nanometers [4].

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As a preliminary step, the parts undergo a water cleaning process in which alkaline surfactants, and sequestering salts are used in order to act as oil degreasers and removers of other dirt from the manufacturing operations. The water resulting from these operations is a fluid containing concentrations of metals, organic load, suspended solids and residual concentrations of the applied chemical agents, which should be discarded when they no longer meet the product quality specifications. This wastewater constitutes the industrial effluent and must be treated in order to attend the legal limits of disposal to the environment.

Coagulation/flocculation is the most applied treatment worldwide in metal-mechanical industries in the electronics sector [5]. Applied reagents are iron and/or aluminium salts and flocculating polymers, which promote the formation of aggregates (flocs), allowing the removal of suspended particles and metallic precipitates by sedimentation or dissolved air flotation [6–9]. However, in the treatment of this effluent, there are cases of non-conformities in relation to the organic load, usually measured in terms of chemical oxygen demand (COD). This situation results from factors such as the oscillation of production and the implementation of programmes to reduce water consumption, which decrease the volume of discarded water, but, on the other hand, increase the concentration of pollutants, and reduce the removal efficiency of soluble organic components.

Furthermore, the treatment of effluents generated by the application of nano-ceramic coatings lacks of systematic studies for the development of the process. Only one study was found which was conducted with simulated effluents on a laboratory scale with the application of nanofiltration membranes [10]. However, processes with membranes can be limited by technical, operational, and economic aspects in full-scale systems with real effluents containing suspended solids. More studies aiming at the treatment efficiency of this type of effluent are important, especially on an industrial scale, for the development of economically and environmentally viable processes and techniques for the industry.

The application of integrated processes, before or after conventional treatment by coagulation/flocculation, called complementary processes, are potential alternatives to improve the quality of the effluent to be discarded. An alternative is the use of the adsorption process with activated carbon, a commercial adsorbent of easy access, which has traditionally been applied to the removal of odour, taste, colouring, and pollutants from water [11–18]. Most studies using activated carbon for pollutant removal use its granular form (GAC) due to its adaptive functionality for continuous contact in packed bed reactors. However, the surface area susceptible to the removal of pollutants is substantially smaller [19,20]. In turn, powdered activated carbon (PAC) has a higher adsorption capability, but the separation of the material after contact with the effluent requires adaptations to the process [9,19]. These adaptations may include the use of flocculated activated carbon in fluidized bed reactors [21,22] or the integration of PAC into the coagulation/flocculation process [23].

In this context, the main objective of this work was to promote improvements in the industrial wastewater treatment plant of a metalworking company in the sector of electronic equipment (air conditioning systems) with the addition of PAC prior to the coagulation/flocculation system currently employed, to meet the legal standards of effluent emission. Comparative studies in terms of process capability were carried out considering the processes of coagulation/flocculation and adsorption/coagulation/flocculation in terms of COD removal. Additionally, the efficiency of the process was monitored considering the emission parameters required by the environmental agency and toxicity data with microcrustaceans (*Daphnia magna*) and fish (*Pimephales promelas*). Finally, the benefits achieved considering the modification of the industrial effluent treatment system are discussed.

2. Materials and methods

2.1. Effluent

The investigation was conducted in an air conditioning equipment manufacturing plant located in southern Brazil. The effluent comes from the removal of the protective film of the galvanised plates and the operation of the nano-ceramic coating application process. Basically, it is an aqueous solution that contains dissolved metals (such as chromium, copper, lead, zinc, aluminium and nickel), soluble and insoluble oils, and chemicals used in this treatment, such as potassium hydroxide (KOH), potassium tetraborate ($Na_2B_4O_7·10H_2O$) tetrahydrated, decane ($C_{10}H_{22}$), octenylsuccinic acid ($C_4H_6O_4$), nitric acid (HNO_3) and hydrogen hexafluorzirconate (HF_7Zn). There are also, in a smaller percentage, surfactants employed in cleaning floors and during micro leaks test procedures. The average effluent flow generated is 120 m^3 $week^{-1}$.

2.2. Reagents

The commercial reagents used were: defoaming agent – 40% polydimethylsiloxane in aqueous solution, coagulant – 24% of aluminium polychloride (PACl) in aqueous solution, and an anionic flocculant – high molecular weight polyacrylamide (PAA), all supplied by Quimatex (Brazil). The vegetal-based adsorbent PAC, supllied by Matryx (Brazil), presented a wide granulometric distribution, ranging from 40 nm to 100 μm, with 90% of the particles below 62 μm. Table 1 depicts the main parameters of PAC characterization. Supplementary data (SD 1) also presents the analytical reports of size distribution analysis (laser diffraction technique, equipment Cilas® 1064) and BET specific surface area (Quantachrome® Nova Station A) of the sample of PAC employed in this study.

Table 1
Characterization of the adsorbent powdered activated carbon (PAC) used in the study

Raw material	*Pinus elliottii*
Specific surface area (m^2 g^{-1})	424
Mean diameter (μm)	30.9
Specific mass (g cm^{-3})	1.49
Moisture (%)	10
pH_{PZC}	7.3

The PACl and the flocculant polymer were prepared at stock concentrations of 70 g Al L^{-1} and 0.35 g PAA L^{-1}, respectively. pH adjustment is not usually necessary, since the pH of the final effluent usually lies between 8.5 to 9.0, which is within the established emission limits (between 6.0 and 9.0).

2.3. Definition of the operating conditions of use of the PAC

Operating conditions of PAC usage in the industrial effluent treatment was defined in laboratory trials, using jar test equipment (Quimis, Q305, Brazil), with jar volumes of 1 L. A representative sample of the effluent was collected in the equalisation tank of the industrial treatment plant, after homogenisation and before the addition of the defoaming agent. From this initial sample, a volume aliquot of 1 L was separated for COD analysis of the raw effluent, and the remainder was used for the bench scale tests for the definition of the optimum dosage of PAC, contact time, and the effect of pH. All tests were conducted with fixed conditions of defoaming agent dosage (0.25 g L^{-1}) and stirring rotation of 30 rpm.

Initially, for the definition of the best PAC dosage, a contact time (agitation) of 1 h was fixed at the rotation of 30 rpm. The process was monitored with pH measurement using the pH meter AK 103 AKSO and, in this condition, the pH remained at 8.9 +/– 0.1. In the studies referring to the PAC/effluent contact time, a fixed dosage of 0.5 g L^{-1} of PAC was used. Finally, the study of the pH effect was conducted with 0.5 g L^{-1} of PAC and contact time of 1 h, with pH adjustment using solutions of hydrochloric acid ([HCl] = 0.1 M) or sodium hydroxide ([NaOH] = 0.1 M). Table 2 shows the levels of parameters studied in the bench top scale process. In all cases, the treated effluent sample was filtered, cooled (4°C), and sent for COD analysis.

2.4. Effluent treatment on industrial scale

The effluent treatment was performed in weekly batches according to the company's routine. Fig. 1 shows, schematically, the wastewater treatment plant (WWTP). The conventional treatment method included the addition of a defoaming agent, the coagulation/flocculation process, and the separation/clarification by sedimentation, obtaining a treated effluent stream and a sludge, which goes through thickening and filtration stages for the separation of the solid phase. The treatment was modified by adding the PAC before the conventional process. The applied protocol was: mixture of the effluent in the equalisation tank for 30 min; addition of the defoaming agent in the same tank at a dosage of 0.25 g L^{-1} and mixing time of 1 h; when applied, the addition of PAC in the equalisation tank in a dosage of 0.5 g L^{-1} and mixing for 4 h; addition of polyaluminium chloride in the rapid mixing unit in a dosage of 130 mg Al^{3+} L^{-1} and mixing time of 1 h and 30 min; addition of flocculant polymer in the slow mixing unit, at a dosage of 2 mg L^{-1}; clarification of water by sedimentation and thickening and filtration of the generated sludge, with disposal of the clarified product to the receiving water body. For the quantification of the sludge generated in each batch, a sample of 1 liter of effluent was collected in the slow mixing unit. The sludge was filtered, the retained solids were dried in a heating chamber at a constant temperature of 60°C, and the total mass quantified considering the volume of effluent brought to treatment. During effluent treatment studies at the industrial scale, 14 batches were performed according to the conventional process and 14 batches with the condition of pre-treatment with PAC followed by the conventional process.

Table 2
Bench scale study optimization parameters (jar test)

Parameter	Studied levels	Fixed parameter
PAC (g L^{-1})	0 - 0.25 - 0.5 - 1.0 - 1.5	Contact time = 1 h pH = 8.9 (+/– 0.1)
Contact time (h)	0.5 - 1 - 2 - 4 - 6	PAC = 0.5 g L^{-1} pH = 8.9 (+/– 0.1)
pH	2 - 3 - 4 - 5 - 6 - 7 - 8 - 9 - 10 - 11 (+/– 0.1)	PAC = 0.5 g L^{-1} Contact time = 1 h

The samples of the raw industrial effluent were collected directly in the WWTP equalisation tank, after homogenisation and before the addition of the defoaming agent, and the treated effluent in the Parshall flume that measures the effluent outlet flow. Samples were kept refrigerated at 4°C and sent for analysis on the same day. The analyses carried out on the industrial effluent were the same as those established in the environmental operating license, according to environmental regulations: pH, phenols, sedimentable solids, suspended solids, COD, total Kjeldahl nitrogen, ammoniacal nitrogen, total phosphorus, sulphides, surfactant substances, aluminium, lead, copper, chromium, nickel, zinc, oils, and greases. All methods of analysis were performed according to the "Standard Methods for Water and Wastewater Analysis" [24] using analytical grade reagents. The main parameter of the polluting potential of the effluent used in this study was the COD, estimating the biodegradable and non-biodegradable organic load, which was conducted by the 5220 D method [24]. The acute toxicity analysis, performed with the test organisms *Daphnia magna* and *Pimephales promleas*, were conducted according to ABNT NBR 12713/2016 [25] and 15088/2016 [26] in 4 random treatment batches considering the raw effluent as well in those treated with and without PAC. Results of the observed effects were expressed as toxicity factor (TF) that corresponded to the lowest dilution which produced immobility or death up to 10%. The result was expressed in integer equivalent to the test solution's dilution factor.

2.5. Statistical processing of data

The set of COD results were evaluated by statistical basic parameters as mean (X) and standard deviation (σ) as well through the process capability (Cp). In this case, when the process characteristic is of less-is-better type, the lower specification limit (LSL) is theoretically zero maintaining as determinant the upper limit specification (ULS) and the superior Cp applying Eq. (1) [27]:

$$\mathrm{Cp}_{\mathrm{sup}} = \frac{\mathrm{ULS} - X}{3\sigma} \tag{1}$$

where X is the arithmetic mean of the values found, ULS is the upper limit of the specification, σ is standard deviation of the sample and upper Cp.

The focus was to evaluate stability and improvement actions in the process. The relationship between capability, Cp index, and statistically estimated amount (%) of non-conformities are summarised in Table 3.

The results obtained in the statistical calculations were compared with the maximum emission specification values established by the environmental agency, in this case a COD value of 330 mg L^{-1}. The process capability was applied to the COD results in the two conditions of industrial effluent treatment – with and without PAC.

3. Results and discussion

Initially, laboratory studies were conducted to establish the best condition of use of the PAC. It was observed that the removal of COD increased substantially with the amount of PAC applied up to the amount of 0.5 g L^{-1}. From this dosage, removal continues to grow, but at lower increments. For example, with the addition of 0.5 g L^{-1} of PAC the removal of COD was 53%. By doubling the amount of PAC to 1.0 g L^{-1}, COD removal was 58%. Therefore, the chosen concentration of adsorbent, under the conditions of this study, was determined to be 0.5 g L^{-1}. Regarding the conditioning time of the PAC, a period of 1 h is sufficient for the system to come into equilibrium. Concerning pH, the process has a slightly better efficiency in a slightly alkaline medium, between pH 8 and 10, with no great variation in this range. This favours the process, since the effluent is already in this pH range. A summary of the results obtained in the laboratory studies is shown in Table 4.

Bench scale studies served to define an adequate PAC dosage for application in the full-scale tests. Table 5 presents the average values referring to the raw effluent, the full-scale treatment by coagulation/flocculation, the full-scale treatment by adsorption/coagulation/flocculation, and the emission standards required by the environmental agency. During the test time period, the pH values of the treated effluent remained in the range of 7.0 to 8.9 and the temperature close to 20°C. It can be observed, by the average values, that the raw effluent does not meet the standards of organic matter, including COD, biochemical oxygen demand (BOD), oils, and greases. It also does not meet the standards for Zn and sulphides. After treatment by coagulation/flocculation, at least considering the medium values, all emission standards were met. However, it appears that the COD parameter has an average value bordering on the maximum emission limit with cases of non-conformities. Analysing a 5-year history, there are approximately 10 non-conformities for every 100 batches of treatment. Non-conformities are associated with variations in the discarded effluent from

Table 3
Scale for the evaluation of process capability

Capability	Cp	% out of specification
Very incapable	0.33	32
Unable	0.66	4.4
Capable	1.00	0.27
Very capable	1.33	0.0064
Extremely	1.67	0

Source: Kume [27]

Table 4
Conditions established in laboratory studies for the use of PAC in effluent pre-treatment

Condition	Result
PAC dosage (g L^{-1})	0.5
Stirring time (h)	Minimum of 1 h
pH	with a variation of less than 5% between pH 5.0 and 10.0

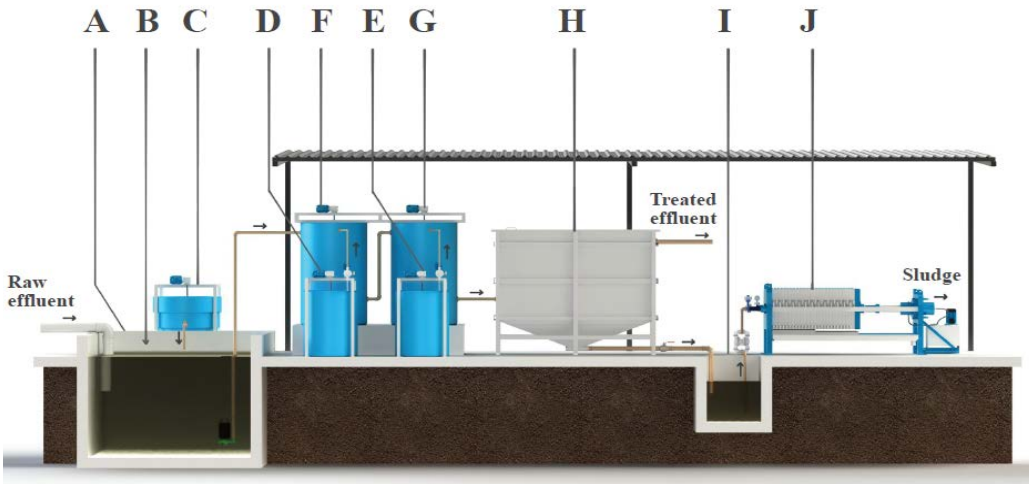

Fig. 1. Wastewater treatment plant: (A) equalisation tank; (B) defoaming dosing point; (C) activated carbon dosing point; (D) coagulant preparation; (E) flocculant preparation; (F) rapid mixing unit; (G) slow mixing unit; (H) clarification basin; (I) sludge thickener; (J) filter-press.

the industrial plant, which the conventional treatment procedure is not able to assimilate. Eventually, it is not possible to discharge the effluent into the receiving water body, and there is a need to re-submit it to treatment in order to meet the adequate conditions for disposal. However, the addition of PAC to the process improved almost all parameters evaluated. In the case of COD, reduction was from 265 mg L^{-1} after coagulation/flocculation to 127 mg L^{-1} after adsorption/coagulation/flocculation.

The COD values of the treated effluent at each batch operation, considering before and after the corrective action of PAC addition, are presented in Fig. 2. The statistical evaluation of the process capability in relation to this parameter clearly shows the improvement action provided by the PAC in the quality of the final effluent (Table 6). Conventional treatment by coagulation-flocculation presents a Cp of 0.55, which indicates the process as "unable" to COD removal. With the addition of PAC, the Cp value passes to 1.13, framing the system as "capable".

To consolidate this information, a nominal scatterplot (Fig. 3) was drawn for treatments in situations with and without PAC, making evident the gain in stability and

Table 5
Mean and standard deviation of the physical and chemical properties of the raw and treated effluent on an industrial scale (considering coagulation/flocculation and adsorption/coagulation/flocculation) as well as the removal efficiency

Parameter	Raw effluent ($n = 28$)		Treatment by coagulation/flocculation ($n = 14$)			Treatment by adsorption/coagulation/flocculation ($n = 14$)			Upper limit for the emission
	Mean	Standard deviation	Mean	Standard deviation	Mean efficiency	Mean	Standard deviation	Mean efficiency	
	(mg L^{-1})		(mg L^{-1})		(%)	(mg L^{-1})		(%)	(mg L^{-1})
COD	1,323	235	265	39.4	80	127	52.7	90	330
BOD_5	473	67	95	39.4	80	46	52.7	90	120
Oil and grease	57	33	<10	–	–	<10	<10	–	10
Phosphor	0.97	0.7	0.29	0.21	70	0.27	0.31	73	3
Total Kjeldahl nitrogen	9.83	4.6	<5	–	–	<5	–	–	20
Ammoniacal nitrogen	<5	–	<5	–	–	<5	–	–	20
Lead	<0.006	–	<0.006	–	–	<0.006			0.2
Copper	0.61	0.6	0.04	0.004	93	0.02	0.02	96	0.5
Nickel	0.1	0.11	0.01	0.003	89	0.01	0.003	89	1
Zinc	4.15	3.32	0.15	0.09	96	0.13	0.07	97	2
Sulphides	0.5	0.5	0.10	0.01	79	0.08	0.05	83	0.2
Aluminium	5.6	5.9	1.29	0.49	77	1.26	0.49	78	10
Chrome	<0.009	–	<0.009	–	–	<0.009	–	–	0.5
Anionic surfactants	1.22	0.30	0.3	0.12	075	0.26	0.11	78	2
Phenol	<0.04	–	<0.04	–	–	<0.04	–	–	0.1

Average pH of 8.7 for raw effluent and 7.6 for treated effluent.

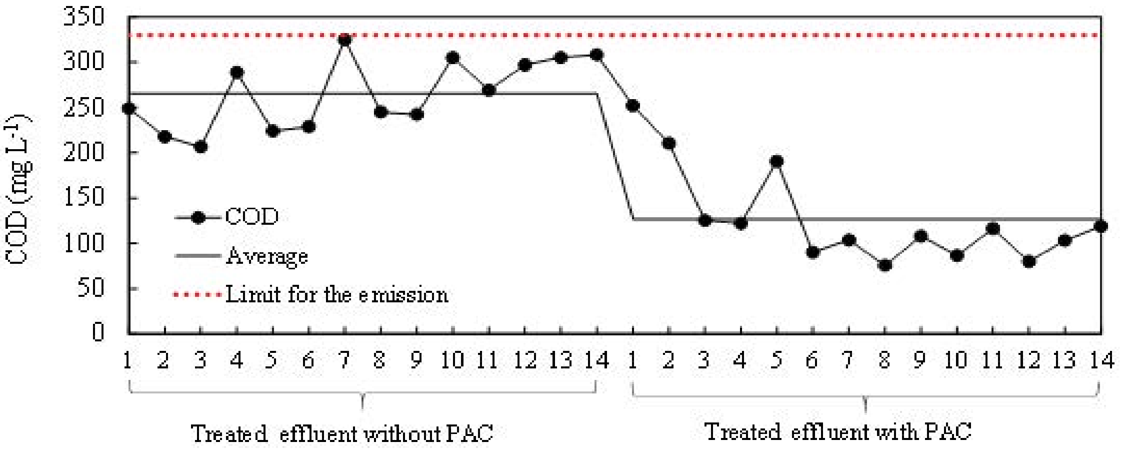

Fig. 2. Residual COD values per batch of treatment considering the effluent treated by coagulation/flocculation and after the introduction of PAC in a heteroaggregation system by adsorption/coagulation/flocculation.

Table 6
Evaluation of the process capability for removing COD in an industrial plant according to the two conditions of treatment of the effluent: coagulation/flocculation and adsorption/coagulation/flocculation

Condition	Effluent treated without PAC	Effluent treated with PAC
Limit (mg L^{-1})	330	330
Mean (mg L^{-1})	265	127
Standard deviation	39.4	52.7
Interval (mg L^{-1})	242.3–308.3	252.1–86.7
Non-conformities	1 (n = 14)	0 (n = 14)
Cp	0.55	1.13
Cp limit	1	1
Capability	Unable	Capable

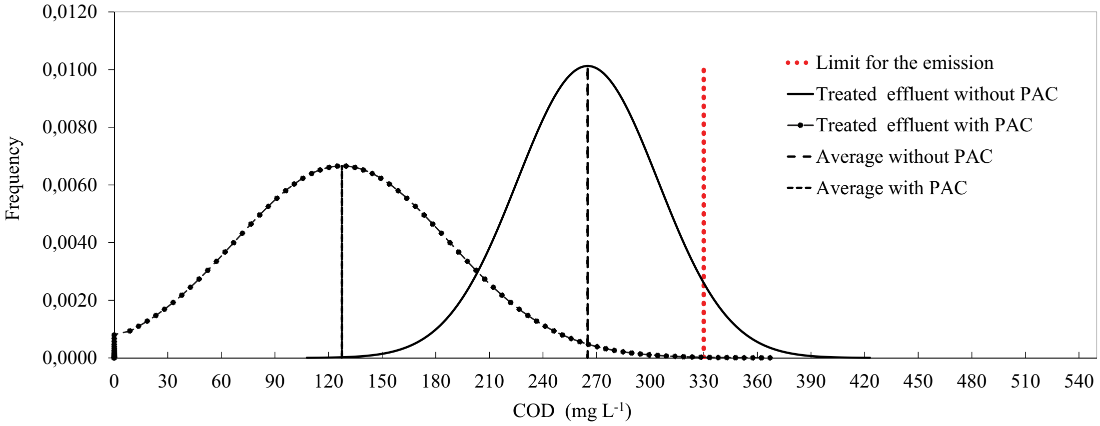

Fig. 3. Normal dispersion of industrial effluent treatment results in an industrial plant with and without PAC adsorption.

Table 7
Range of toxicity factor of the raw effluent and after the treatment considering simple coagulation/flocculation and adsorption/coagulation/flocculation (n = 4)

Parameter	Range of toxicity factor – TF		
	Rough effluent	Effluent treated without activated carbon	Effluent treated with activated carbon
Pimephales promelas	8–32	16–32	1–2
Daphnia magna	64	8–64	1–4

removal of COD in the effluent treatment when the adsorption process was introduced. With conventional treatment, the value of the 3-sigma exceeds the emission limit established by legislation, a condition that indicates an out-of-control process. On the other hand, when the adsorption process is integrated into the system, the values of the 3-sigma were below the legal limit indicating a process condition under control.

Improvements can also be observed in relation to the toxicological index. The raw effluent has a TF values ranging from 8 to 32 for the fish *Pimephales promelas*. After the treatment by coagulation/flocculation, the toxicity is similar, with values between 16 and 32. However, after the treatment by adsorption/coagulation/flocculation, the value TF fell to the interval 1 to 2. A similar situation occurs for the microcrustacean *Daphnia magna*, where the gross values of TF go from 64 to the range of 8 to 64 for the effluent treated by coagulation/flocculation, and to the range of 1 to 4 after the treatment by adsorption/coagulation/flocculation (Table 7).

The addition of PAC is reflected in the generation of sludge. Without PAC, the average generation was 0.30 g of solids per L^{-1} of wastewater. After the addition of PAC, average sludge generation changes to approximately 0.8 g L^{-1}, which represents a proportional cost in forwarding the material for co-processing in cement plants. However, operationally, the procedure was adopted due to the benefits obtained in relation to the quality of the treated effluent.

It is also worth mentioning that a survey was carried out in the air conditioning equipment production sector in order to learn about the types of effluent treatment applied [5]. A questionnaire was applied to 20 companies in the sector - ten from South America, five from Asia, four from

Europe and one from Africa, resulting in an 80% return. Within these companies, 56% perform the conventional treatment by coagulation/flocculation followed by a final polishing step by adsorption with granular activated carbon (GAC), 19% treat the effluent only by coagulation/flocculation and 25% subcontract the wastewater treatment to elsewhere or are unaware of the applied process.

The use of GAC in fixed bed filters, after treating the effluent by coagulation–flocculation and sedimentation, is a common practice in companies in the metal-mechanical sector and has already been applied in the company where this study was carried out. However, our experience is that this practice is associated to operational problems related to the obstruction of the filter columns, the need to change the GAC bed in short periods of time due to saturation, and a high generation of solid waste ended up becoming impediments to the application of this process configuration.

In this study, the use of PAC was performed prior to the coagulation–flocculation stage and the mechanisms involved were the adsorption of dissolved organic pollutants onto PAC particles, followed by the aggregation of the PAC and the suspended solids presented in the effluent, generating large and resistant flocs that presented a favorable settling rate. This practice is not usually adopted in the treatment of effluents and may be an option in the industrial sector.

From the results obtained, the use of PAC could be encouraged in the treatment of effluents from the preparation of metallic parts with nano-ceramic coatings. The optimal dosage of PAC is a function of the concentration of dissolved organic carbon in the effluent to be treated [11,28]. Thus, in events of great fluctuation in the concentration of organic load at the feed of the effluent treatment plant, this parameter must be adjusted to maintain the COD removal efficiency and minimise the costs associated with the inputs and disposal of process sludge. Altmann et al. [11] pointed out dosages in the order of 0.5 mg_{PAC}/mg_{COD} for the removal of drugs and pesticides dissolved in water. Herein, the average ratio was in the same range of magnitude, with a value of 0.4 mg_{PAC}/mg_{COD}. The amount of PAC per unit of effluent volume used in this work, of 0.5 $g\ L^{-1}$, is in a range of magnitude similar to those applied to effluents from other industrial sectors. Reported studies on the use of PAC in effluents (industrial and urban) containing organic micro pollutants, dyes and surfactants, have shown PAC dosages ranging from 0.25 to 2 $g\ L^{-1}$ [11,17,18,28]. Li et al. [13] carried out a study of landfill leachate treatment, where the optimal PAC dosages in the adsorption tests point to values of 10 $g\ L^{-1}$, with 86% removal of COD.

The use of PAC in removing emerging pollutants from surface or underground waters for public supply and domestic effluents has been the subject of successful investigations [12,13,16,29,30]. The application of PAC in the treatment of effluents to remove organic micropollutants has shown that the presence of suspended solids does not significantly affect the adsorption capability of the dissolved pollutants [31].

Additionally, some authors report several benefits of using PAC in stages prior to coagulation-flocculation, mainly in the formation of larger, denser, and more resistant flakes, providing, among other advantages, higher rates of sedimentation, removal efficiencies and process capabilities [14,15]. Yet, Krahnstöver and Wintgens [23] presented a review of the processes used to separate the PAC during treatment. According to these authors, after the adsorption step in stirring reactors with PAC, dosages of Al^{3+} or Fe^{3+} equivalent to 0.1–0.4 $mg_{metal}\ mg_{PAC}^{-1}$ and flocculant dosages of the order of 0.3 $mg\ L^{-1}$ are necessary. The dosages applied in this work also fall into this range, having been estimated at 0.26 $mg_{Al3+}\ mg_{PAC}^{-1}$ and 0.25 $mg_{flocculant}\ mg_{PAC}^{-1}$.

4. Conclusion

The production of air conditioning equipment with the application of nanoceramics on metal plates generates an industrial effluent that needs treatment before discharge in the environment. Conventional coagulation/flocculation treatment is not able to assimilate variations in the effluent without presenting non-conformities in relation to COD. In the evaluation of the industrial process, the treatment by only coagulation/flocculation produced mean COD values of 265 $mg\ L^{-1}$. The addition of PAC in the system reduced the average value of the final effluent to 127 $mg\ L^{-1}$. The statistical evaluation of the process capability for COD removal demonstrated that the coagulation/flocculation process has a Cp of 0.55 (not capable) and that adsorption/coagulation/flocculation increased the Cp value to 1.13, making the gain in process stability evident. The other parameters analysed in the industrial effluent, due to the company's operational license requirement, remained below the legal release limits. The benefits of using the PAC were also evidenced in terms of ecotoxicological parameters in fish and microcrustaceans. The end result of the use of PAC in a hetero-aggregation process resulted in environmental and operational improvements for the air conditioning industry. Still, the similarities of the effluent treatment process with that of other industries show that the innovation proposed in this work can be transferred to other sectors of the metal-mechanical industry.

Acknowledgements

The authors are grateful to CAPES, CNPq, UFRGS and Midea Carrier for the financial support for this investigation.

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