IIBCC

Organic matter removal of process water in the fiber cement industry

Mirian Yasmine Krauspenhar Niz[1] and Holmer Savastano Junior

Research Nucleus on Materials for Biosystems (NAP BioSMat), University of São Paulo (USP), Avenida Duque de Caxias Norte, 225, P.O. Box: 13635-900 Pirassununga, São Paulo, Brazil

[1]mirian.niz@gmail.com (corresponding author)

ABSTRACT

The organic matter (OM) contamination in the fiber cement industry can interfere in the reuse of the closed circuit water. To mitigate problems in the production process and in the quality of the final product, treatment alternatives may be required. This study presents a characterization of the process water of three different fiber cement industries in Brazil and an evaluation of alternative treatment routes. From the characterization of the process waters it could be observed that, on average, 98% of the OM present in the process water is soluble and; from 8 to 28% of this OM is biodegradable. Based on that, treatment solutions for soluble non-biodegradable OM were evaluated: (i) pH reduction of the water in the refining process to avoid OM contamination, and (ii) activated carbon adsorption for OM removal. The reduction of the process water pH was carried out by CO_2 insufflation, with the reduction of pH from 12.5 to 7. Thereafter, both waters (before and after pH reduction) were used in a leaching test with cellulose pulp (Kappa 30) and the water with pH 7 resulted 47% lower OM contamination. The adsorption test was held using bituminous activated carbon in a dosage of 1 g/L, in batch mode, at two different pHs (12.5 and 7, respectively). The pH did not impact the adsorption and in 5 h (equilibrium time), 41% of the OM was removed. Both treatments are promising alternatives to solve organic matter (OM) contamination, however, pH reduction in refining process has a greater appeal for avoiding the problem instead of solving it.

KEYWORDS:

Leaching effect, water contamination, active carbon, water reuse.

INTRODUCTION

The reuse of water in the fiber cement industry is conditioned by the quality of the water itself, which can be affected by inorganic and organic compounds. The inorganic contamination problem and treatment alternatives methods were addressed in previous study (Mármol et al. 2018). The organic contamination of process water is assessed in the present research work which was divided in a two-part study.

The origin of organic matter (OM) as well as the effects of this type of contamination in the production process and in the final product was investigated elsewhere (Niz and Savastano Junior, 2021[1a]).

The OM contamination of process water have already shown to interfere in cement setting and hydration process and, when OM contamination of process water reaches an upper limit, not only the production process is affected but also the final product quality decreases (Niz and Savastano Junior, 2021). Therefore, not only monitoring process water is important, but also treatment alternatives to remove OM contamination of process water should be available when and if the upper limit is reached.

Understanding of the nature of wastewater is fundamental to the design and operation of the treatment and reuse facilities (Metcalf & Eddy 2003). Thus, selecting a treatment alternative for the reuse of process water in the fiber cement industry demands a thorough knowledge of its characteristic. The physical and chemical characteristic of the process water can guide the choice of the most appropriate treatment technology and characterization of process water from different industries is essential, either to choose the best technology based in more reliable data or to determinate whether there is a homogeneity of composition, enabling the use of similar technologies in different industries.

The present paper has the objective to evaluate treatments alternatives to remove or avoid the release of organic matter (OM) contamination in the process water of fiber cement manufacturing.

MATERIALS AND METHODS

In order to select the best treatment technology, the characterization of process water from three fiber cement industries in Brazil was carried out. Two treatment alternatives were proposed and evaluated. The first is the pH neutralization of the process water used in the refining process by CO_2 insufflation, as an alternative to reduce the OM contamination by the pulp leaching effect. The second was activated carbon adsorption to remove OM from process water.

Process water characterization

The focus of the present work was the OM contamination. Process water from three different fiber cement industries was evaluated according to the following parameters: Total Organic Carbon (TOC), total and soluble Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), evaluated according to the methodology presented in the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, and WPCF 2005) and BOD/COD ratio. Those parameters enable the evaluation of the OM present in the process water, the solubility condition and the biodegradability potential.

Conductivity and pH were evaluated with potentiometric methods (APHA, AWWA, and WPCF 2005), those parameters are essential for the determination of an appropriate treatment method.

---

[1] Unpublished manuscript to be presented in the IIBCC 2021.

The solid content profile of the process water from one of the industries was also evaluated (total solids, volatile total solids and fixed total solids) to improve the assessment of the feasibility of the proposed treatment method (APHA, AWWA, and WPCF 2005).

To guarantee similar sample conditions, samples collections in the three industries were performed in the same point of the process, the sedimentation tank (cone 2), and after seven days of production running. These sampling conditions are considered as the most critical for the system since water had been recirculated during the whole week of production and collected in the most polluted part of the Hatschek system.

CO_2 insufflation

The neutralization of the pH of the process water was achieved by 20 min CO_2 insufflation as described by Mármol et al. (2018). Neutralized process water with pH of 7 was obtained and used to grind pulp kappa 30 in the leaching test. The characteristics of process water, before and after CO_2 insufflation, are presented in Table 1. The water used in this experiment is not the sample utilized in the characterization experiments.

The leaching test consisted in simulating the refining process in a laboratory scale. The test was held by grinding the pulp with the neutralized process water for 5 min. After grinding, the mix water + pulp was put under mixing (140 rpm) at controlled temperature of 50°C for 24 h. This condition simulates the tanks where the pulp is kept after refining in the industries, before its use in the production process. The leaching was monitored by measuring the OM content (COD basis) in the water with 1, 3, 6, 12 and 24 h of contact between water and pulp.

Table 1 - Process water before and after CO_2 insufflation

Parameters	*Process water*	*Process water after CO_2*
Conductivity (mS/cm)	25.5	24.5
COD (mg/L)	1025	1002
Sulphate (mg/L)	9423	8314

Activated carbon adsorption

Adsorption test were performed in batch mode with powdered bituminous carbon. A complete characterization of the carbon used in the present research can be found elsewhere (Saraiva, 2019).

The first test was carried out to observe the influence of the process water pH in adsorption process and to determinate the equilibrium time, that is, the minimum contact time required between process water and the activated carbon to obtain the maximum removal of the OM.

Two pH conditions were evaluated: alkaline process water (without pH neutralization) and process water with pH of approximately 7 (achieved by hydrochloric acid addition) (Figure 1 A). Thereafter, carbon dosage (1, 2, 4 and 8 g/L) was evaluated, also in batch test, using the information of pH and equilibrium time obtained in the first test (Figure 1 B).

The OM removal was evaluated in COD basis. Samples were collected with 0, 1, 3, 5, 7, 9 and 20 h of contact time in the first test, and with 0, 1, 2, 3, 4 and 5 h of contact time in the second test.

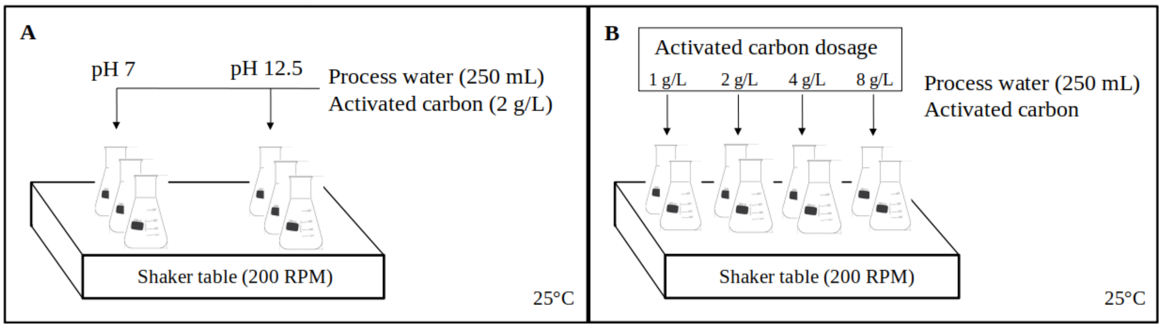

Figure 1 - Experimental setup (A) Equilibrium time and pH test and (B) Carbon dosage test.

RESULTS

Water process characterization

The results of the parameters evaluated for the three process waters can be observed in Table 2. The process waters from the three industries showed similar characteristics concerning the OM composition.

Table 2 - Process water characterization

Parameters	*Industry 1*	*Industry 2*	*Industry 3*
TOC (mgC/L)	291	249	228
Total COD (mgO$_2$/L)	1289	982	912
Soluble COD (mgO$_2$/L)	1233	935	897
BOD (mgO$_2$/L)	320	249	250
BOD/COD (%)	26	27	28
pH	12.6	12.6	12.61
Conductivity (mS/cm)	42	47	49

On average, 98% of the OM present in the process water is soluble, comparing the total COD and the soluble COD values. This result indicate that the organic contamination could not be removed by separation techniques, such as filtration or sedimentation process. As well as biological treatment are not suitable, since the BOD/COD ratio indicate a maximum biodegradability of 28%. That is, if and efficient biological treatment method were applied (which, due to the pH of process water alone, is already a difficult task), only 28% of the OM contamination could be removed.

The solids content of the process water from industry 1 was also evaluated, in order to obtain more information about possible treatments alternatives. The analysis of the solids content enables the accounting of the rapid settleable solids contaminants present in the process water that could not be quantified by the analysis methodologies mentioned above.

Total solid content of process water from industry 1 was 32 g/L of which 30 g/L were inorganic compounds (fixed total solids, i.e. solids that remained after sample drying at 560°C for 30 min). The volatile portion represents the organic portion of the solids (Metcalf & Eddy, 2003), that is 2 g/L. This value is almost to times greater than the total COD observed in the process water. Thus, regardless the treatment method to be applied, a sedimentation tank before OM removal treatment is recommended to avoid overburdening.

CO_2 insufflation

The water pH seems to play an important role in the leaching effect (alkaline extraction of lignin) and possibly, if the pH of the water used in the refining process could be decreased or even neutralized before this process, the leaching could be minimized and consequently the OM contamination. To test this hypothesis, a leaching test was performed with pH neutralized process water.

Insufflation of the process water with CO_2 promoted neutralization of the pH (from 12.5 to 7.1), reduction of 11% on the sulphate content and approximately 2% of COD reduction. During insufflation, it was possible to see precipitation of some components. Observing the change in the conductivity from 25.5 mS/cm to 24.5 mS/cm, is possible to infer that the CO_2 insufflation promoted salts precipitation. Besides that, results of previous experiments with fiber cement process water CO_2 insufflation already demonstrated that mainly $CaCO_3$ and $CaSO_4$ precipitation occurs (Mármol et al., 2018).

When the process water with lower pH was used to grind the pulp, a lower leaching effect was observed, comparatively to the leaching observed when process water (pH 12.5) was used. As it can be seen in Figure 2, after 24 h of leaching test, the increase in the COD in the process water was of 278 mg/L and when the process water with lower pH was used (after CO_2 insufflation), the COD increase was 47% lower (148 mg/L).

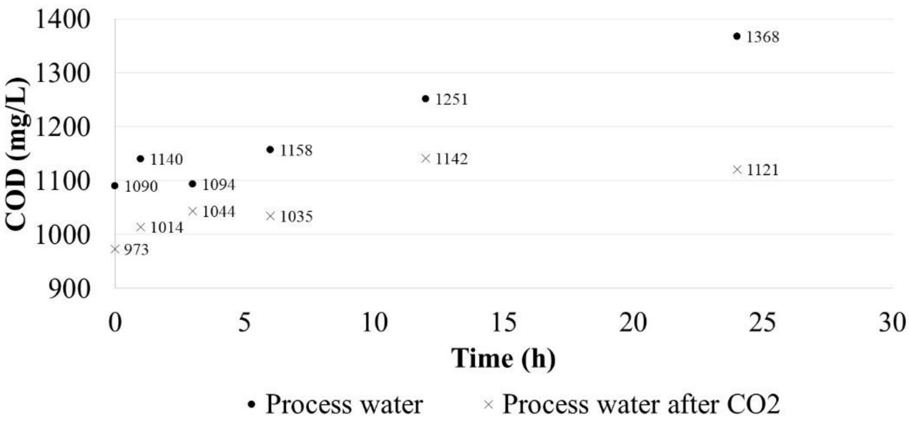

Figure 2 - Chemical oxygen demand (COD) temporal profile during leaching test with process water and process water after CO_2 insufflation.

When pure deionized water was used in the leaching test (presented in the first part of this research – PAPER 1), the leaching resulted in a water COD increase of 152 mg/L. This demonstrates that lowering the pH of the process water before refining process reduces the leaching effect to values similar to those observed when pure deionized water was used. Process water neutralization could be done in the portion of water that is used in the refining process only. A simplified sketch of treatment alternative with CO_2 insufflation is presented in Figure 3.

Previous studies have already shown that a greater efficiency of the refining process can be achieved by applying higher pH media (Bäckström, 2020). However, even though neutralizing the pH of the process water could impact the refining process, this treatment alternative could be considered, given that, avoiding contamination rather than removing it, is a cleaner production strategy with an intelligent management approach. This treatment alternative could be further investigated to determine if lower pH neutralization level (for example: lowering the process water pH to 10 instead of 7) could decrease the leaching effect and consequently OM contamination without impacting the refining process.

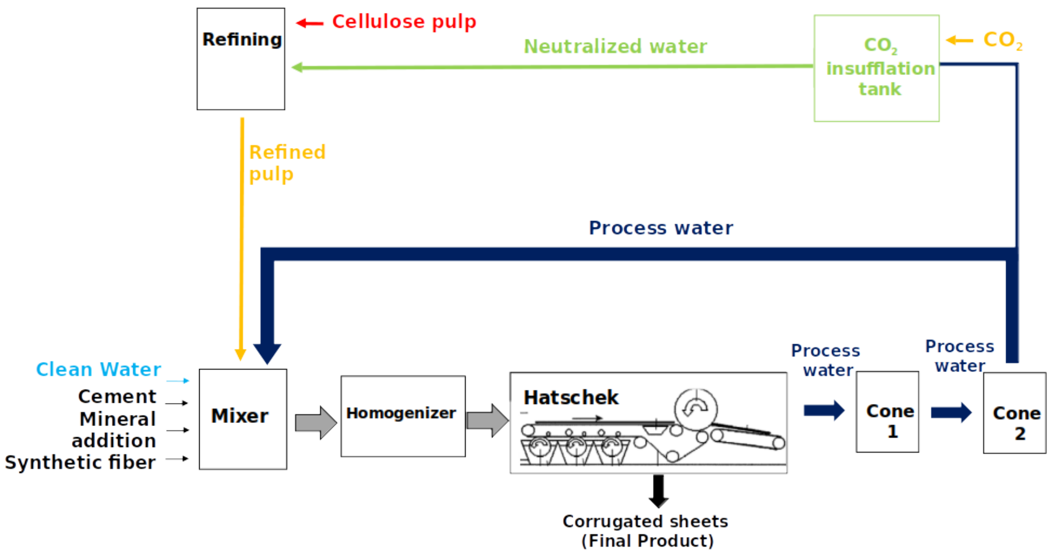

Figure 3 - Simplified sketch of process water treatment alternative by CO_2 insufflation.

Activated carbon adsorption

Adsorption is a process resulting from the retention and accumulation of certain substances (adsorbate) on the surface of a solid (adsorbent). Activated carbon is a well-known adsorbent and have shown to be effective in removing organic contamination from several liquid wastes (Kawamura, 2000).

The results from the first adsorption test, performed to determinate pH influence in adsorption and the equilibrium time are summarized in Figure 4. The pH did not interfere in the adsorption potential of the bituminous activated carbon. Actually, as can be seen in Figure 4, COD content data coincide almost perfectly for both conditions and a maximum COD removal of 41% was observed after 5 h of contact between water and carbon, regardless of the pH condition. Thus, for adsorption treatment with activated carbon, pH neutralization is not necessary for OM removal.

After 5 h, an increase in COD was observed (desorption). Therefore, this was considered the equilibrium time, that is, the ideal contact time between process water and activated carbon.

Lowering the process water pH (from 12.5 to 7) promoted a significant conductivity reduction (from 40 to 32 mS/cm), probably due to salts precipitation during pH reduction. Throughout the adsorption test however, the conductivity increased, which is expected in process with activated carbon addition (Kastening and Heins, 2005; Wang et al., 2018). This behavior demonstrates that adsorption is an efficient alternative for reducing OM contamination, but not for inorganic matter removal. Coupling treatments alternatives for inorganic matter removal (Mármol et al., 2018) and OM removal (presented in the present work) could be the best alternative to obtain a high-quality process water for reuse in the Hatschek process.

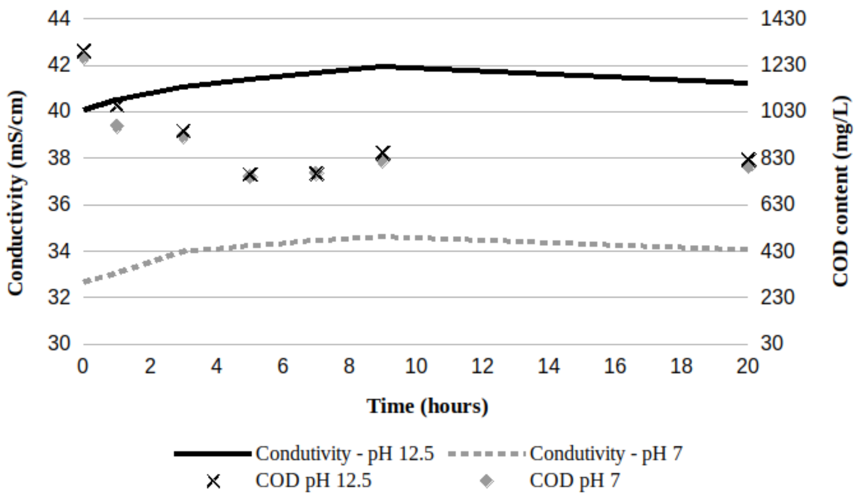

Figure 4 - Equilibrium time and pH adsorption test.

In the carbon dosage test, greater COD reduction was observed with greater dosages. However, the removal rate was not proportional to the carbon dosage (doubling carbon dosage did not double COD removal). With 1 g/L of carbon dosage, a 20% removal was achieved and 60% of COD was removed when the dosage was of 8 g/L (Figure 5). Observing the remaining COD, is possible to conclude that even with the lower carbon dosage, the level of OM content was satisfactory, considering the upper limit that have shown to cause problems to final product quality and production process (Niz and Savastano Junior, 2021).

The adsorption test was held in batch mode, with powdered activated carbon addition in the process water. Powdered activated carbon is usually applied for solving seasonal or sporadic water contamination problems. However, when the problem is recurrent and high doses of powdered activated carbon are required, the use of granular activated carbon columns is more feasible. The advantage of adsorption columns is that there is no need to separate the activated carbon of water after adsorption process, since the activated carbon remains as a fixed column through which water passes.

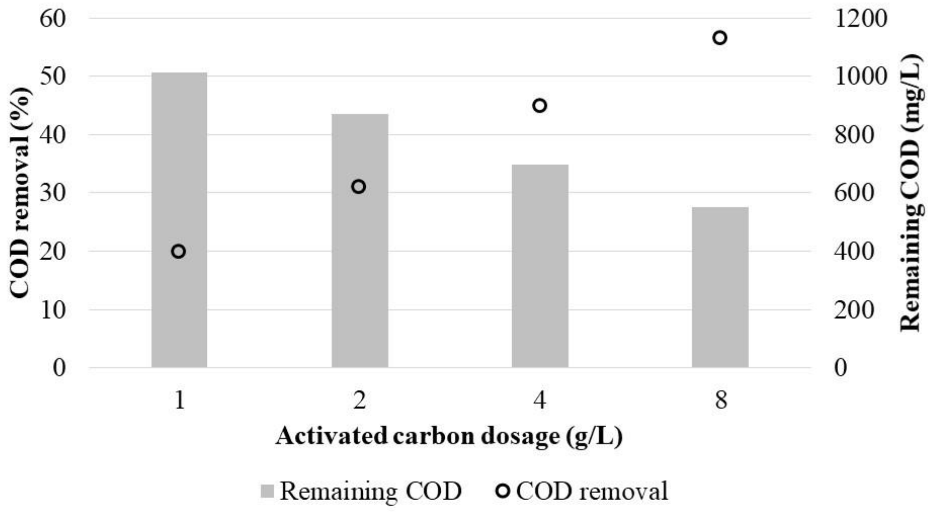

Figure 5 – OM removal and remaining OM content (COD basis) with different activated carbon dosage.

CONCLUSIONS

The process water from the three industries presented similar characteristic of highly soluble OM and low biodegradability. Those characteristics guided the choice of two treatment alternatives. The first one was the impairment of organic matter (OM) contamination by neutralizing the pH of the process water before its use in the refining process of the cellulose pulp, which resulted in lower OM contamination by leaching effect. Although there are potential impacts to refining process associated to neutralizing process water, this is a promising alternative and further investigation is recommended. Due to the soluble non-biodegradable characteristics of OM in the process water, adsorption was the second treatment alternative evaluated. In batch tests with activated carbon, 60% of OM contamination could be removed (in COD basis) when an 8 g/L of carbon dosage was applied, demonstrating a satisfactory removal and a remaining OM content that should not interfere in the production process (based in the results presented elsewhere, Niz & Savastano Junior, 2021). With different approaches, both alternatives have shown to be effective to solve the OM contamination problem.

ACKNOWLEDGMENT

The authors would like to acknowledge the contribution and help of Zaqueu Freitas in the tests performed at the NAP BioSMat Laboratory, the valuable advice from Stephen Akers and the LPB laboratory (*Biological Processes Laboratory*) that facilitated access for the elaboration of the present work. This work was supported by the Brazilian industries: Infibra, Imbralit and Eternit and the financial support from IIBCC.

REFERENCE

APHA, AWWA, and WPCF. 2005. "*Standard Methods for the Examination of Water and Wastewater" 21st Edition*. 21st ed. edited by American Public Health Association. Washington D.C.

Bäckström, Marie. 2020. "*The effect of environment on refining efficiency of kraft pulps"*. Doctoral Thesis. KTH Royal Institute of technology. Stockholm, Sweden.

Govin, A., A. Peschard, and R. Guyonnet. 2006. "Modification of Cement Hydration at Early Ages by Natural and Heated Wood." *Cement and Concrete Composites* 28(1):12–20.

Kastening, Bertel, and Matthias Heins. 2005. "Properties of Electrolytes in the Micropores of Activated Carbon." *Electrochimica Acta* 50(12):2487–98.

Kawamura, Susumu. 2000. *Integrated Design and Operation of Water Treatment Facilities*. Second edi. edited by John Wiley & Sons. New York.

Li, Duan Le, Da Peng Zheng, Dong Min Wang, Ji Hui Zhao, Cheng Du, and Cai Fu Ren. 2018. "Influence of Organic Esters on Portland Cement Hydration and Hardening." *Advances in Materials Science and Engineering* 2018.

Mármol, Gonzalo, Rubén Miranda, Elena D. E. L. A. Fuente, Ángeles Blanco, and Carlos Negro. 2018. "Water Management and Treatment for an Environmentally Friendly Closed Circuit Manufacture." Pp. 41–52 in *International Inorganic-Bonded Fiber Compositics Conference*, edited by H. S. Jr. Cape Town.

Metcalf & Eddy. 2003. *Wastewater Engineering Treatment and Reuse*. Fourth edi. edited by I. McGraw-Hill. New York.

Niz, Mirian Yasmine Krauspenhar and Savastano Junior, Holmer. 2021. *Process water management and the organic matter issue.* Paper to be presented in the IIBCC 2021 (unpublished manuscript).

Saraiva, Matheus Gimenz. 2019. "Post-treatment of textile industry wastewater by adsorption with granulated activated carbon for COD and color removal." *Universidade De São Paulo. Escola De Engenharia De São Carlos* (in Portuguese).

Wang, Tao, Dong Zhang, Lingling Dai, Bin Dong, and Xiaohu Dai. 2018. "Magnetite Triggering Enhanced Direct Interspecies Electron Transfer: A Scavenger for the Blockage of Electron Transfer in Anaerobic Digestion of High-Solids Sewage Sludge." *Environmental Science and Technology* 52(12):7160–69.