

WATER MANAGEMENT AND TREATMENT

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EXECUTIVE SUMMARY

This report includes the hexavalent chromium (Cr(VI)) removal from industrial fiber cement process water. The results include the application of sand filtration columns for the removal of cement-attached Cr(VI) and the application of adsorption treatments for the removal of dissolved chromium. In the first case efficiencies of 90% can be achieved by commercial sands. In the second case, conventional adsorbents as well as novel nanocellulosic adsorbents have been studied. Among the tested materials, the best results are achieved with granular and powdered activated carbons as well as with hairy cellulose nanocrystals, which reach more than 95% of chromium removal under optimal conditions. The techno-economic analysis of the adsorption technologies considers the total costs of conventional process in a wide interval of flowrates. Furthermore, the minimal dosage of hairy cellulose nanocrystals to be considered competitive with respect to conventional treatments has been calculated for pilot/industrial scale implementation. Both the excellent removal efficiencies achieved with hairy cellulose nanocrystals for different industrial process waters, and its easier implementation show the potential of this alternative treatment for the removal of Cr(VI) from process waters of the fiber cement sector.

KEYWORDS

Fiber cement process water, hexavalent chromium, adsorption, nanocellulose, hairy cellulose nanocrystals

PERIOD

2019–2022

PROJECT CONTEXT AND OBJECTIVES

The accumulation of hexavalent chromium in closed process water circuits in fiber cement industries has become a potential health and environmental risk that could also affect the final product. The objective of the project is the removal of hexavalent chromium from fiber cement process waters, analyzing potential solutions to solve this challenge at industrial scale using commercial and novel approaches.

The first study was focused on the treatment of process water where the Cr(VI) was attached to suspended solids like cement. The designed treatment consisted of the application of sand column filtration-adsorption processes in batch-cycle operation. Cr(VI) was measured by spectrophotometry following Standard Method 3500-Cr-B. A total of 30 bed volumes were treated below the limit of discharge and more than 90% Cr(VI) removal was achieved. The second study was focused on the treatment of process waters with high concentration of dissolved Cr(VI) by adsorption. Conventional commercial adsorbents as well as novel nanocellulosic adsorbents were tested. Among these materials, the treatment of real industrial process waters from different companies with granular and powdered activated carbons (GAC and PAC) and hairy cellulose nanocrystals (hairy CNC), seen on figure 1, reached up to 95% of Cr(VI) removal under optimal conditions for almost all the tested process waters. These adsorbents operate following different mechanisms, as shown in figure 2:

- a) Conventional adsorbents (GAC and PAC) adsorb Cr(VI) and need an adsorbent recovery step at the end of the operating cycle.
- b) Novel adsorbents (hairy CNC) show a simultaneous adsorption-reduction of Cr(VI) and can be directly applied without recovery

as they can be used as reinforced nanofiber and, as consequence, generating zero waste. In both cases, the implementation of this treatment is intended to be installed as an intermediate step before the process water is recycled to the production process. A techno-economic feasibility study was performed considering the optimal dosage of each material and the overall conventional process cost estimation (adsorption columns and backwashing treatment train). The backwashing treatment configuration was crucial for the economic viability of the process. The inclusion of sequential two-reverse osmosis treatment train (backwashing water and reject) dealt with half costs compared to a reverse-osmosis-vacuum evaporator treatment, even including fuel cost reduction due to steam production. The flowrate-unit total cost was reduced and stable when the flowrate was lower than $100 \text{ m}^3 \cdot \text{h}^{-1}$. Once implemented, the highest part of variable costs would correspond to the management of chromium-concentrated reject from the final treatment (evaporator or second reverse osmosis).

In the case of hairy CNC, as this material is still not commercial, a minimal cost of implementation was calculated. This cost was lower than $100 \text{ US}\$ \cdot \text{kg}^{-1}$ hairy CNC for pilot and small water treatment plants, while its implementation in long scale facilities becomes favored compared to conventional process, with prices below $20 \text{ US}\$ \cdot \text{kg}^{-1}$.

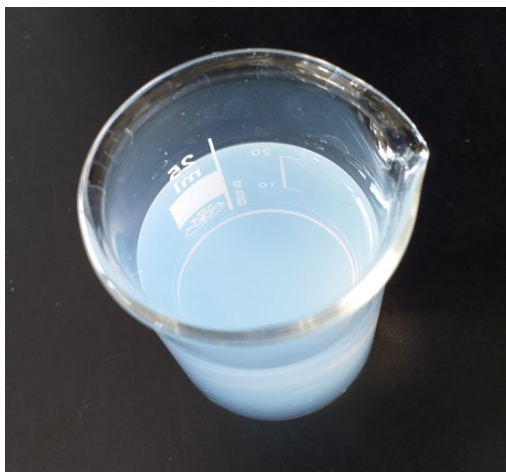


Figure 1. Hairy CNC sample

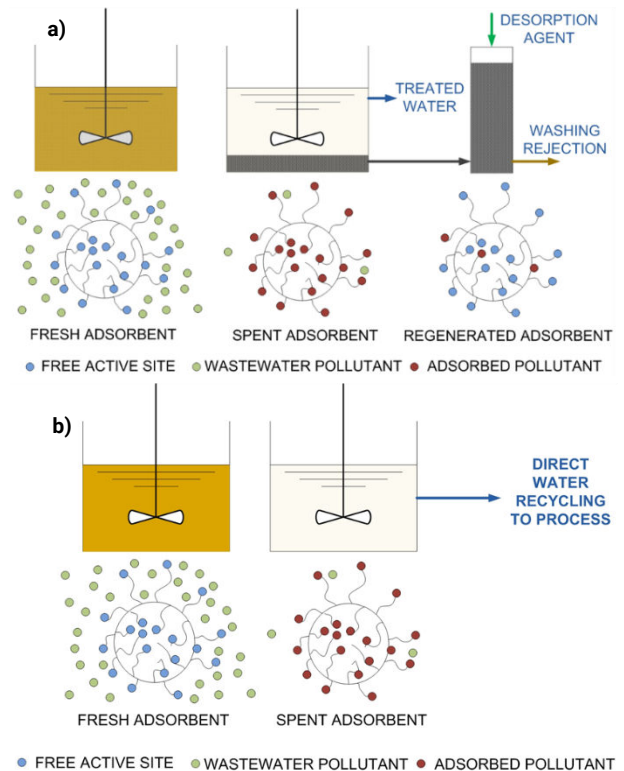


Figure 2. Batch adsorption through a) conventional and b) nanocellulose adsorbents

ACHIEVEMENTS

Several remarkable achievements have been obtained during this project:

- A kinetic model was applied to predict salt adsorption on sand columns. This will allow to better control the treatment.
- More than 90% cement-attached Cr(VI) removal was obtained for long batch treatments with sand columns.
- 95% of dissolved Cr(VI) was removed with GAC, PAC and hairy CNC materials.
- The adsorption of Cr(VI) was the removal mechanism of activated carbons while the adsorption-reduction of Cr(VI) to Cr(III) was the removal mechanism of hairy CNC.
- Overall conventional process was cost-effective under two-reverse osmosis configuration.
- Long-scale implementation of hairy CNC treatment could be economically feasible below $20 \text{ US}\$ \cdot \text{CNC kg}^{-1}$

CHALLENGES

Proof of concept to assess the effect of hairy CNC on the materials to confirm that their direct application improves final product properties.

DURABILITY OF THIS PROJECT AND ITS RESULTS

The results of the project are promising, and the next steps should be the implementation of scaled-up processes from lab to pilot which would confirm the obtained results.

IMPLICATIONS FOR THE INDUSTRY

One of the key factors of this project is the adaptation of the solution to different factories where the Cr(VI) contamination can be present in solution or adsorbed on the cement particles. High removal yields can be achieved with easily implementable processes in both cases.

The advances of the project involve a new technology based on sustainable and non-toxic nanomaterials to prevent the reduction of fiber cement quality due to overconcentration in Cr(VI). This process shows simplicity of installation compared to the conventional process and it has demonstrated its capability to remove this contaminant in waters from different factories, so it could be a solution for a wide variety of sites in the sector. The results also cover the economic impact of this solution, which is also extremely useful for companies evaluating the step from R&D conception to further scaling.

DISSEMINATION

Online presentations:

- IIBCC Connect 2021. Process water treatments for the fiber cement industry. M. Niz. University of Sao Paulo, Brazil. B. Ojembarrena, University of Madrid, Spain

Documents:

- Interim report IIBCC (2020). Water management and treatment. Borja Ojembarrena, E. Fuente, A. Blanco and C. Negro. University Complutense of Madrid, Spain

The results of this project will be shown in different communications in IIBCC 2022:

- Oral presentation: Technical-Economic assessment on the removal of hexavalent chromium from fiber cement process. B. Ojembarrena, University Complutense of Madrid.
- Full paper: Technical and economic assessment of hexavalent chromium removal from wastewater. B. Ojembarrena, University Complutense of Madrid.
- Research poster: Cr(VI) removal from fiber cement process waters using commercial and novel nanoadsorbents. B. Ojembarrena, E. Fuente, A. Blanco and C. Negro. University Complutense of Madrid

In addition, 1-2 scientific papers are expected to be published in high-impact journals soon, dedicated to generating new knowledge in the field of application of adsorption treatments to process water in fiber cement industries, hexavalent chromium removal from this water streams, the technical and economic assessment of the adsorption processes and the novelties in the use of hairy cellulose nanocrystals in wastewater treatment for industrial applications.

FEEDBACK ON THE IIBCC-SPONSORED RESEARCH PROJECT

This IIBCC-sponsored research work was presented at the IIBCC 2022.

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