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TECHNICAL AND ECONOMIC ASSESSMENT OF HEXAVALENT CHROMIUM CONTAMINATION OF WASTEWATER

BORJA OJEMBARRENA, ELENA DE LA FUENTE, ANGELES BLANCO AND CARLOS NEGRO

University Complutense of Madrid, Department of Chemical Engineering and Materials, Avda. Complutense s/n. 28040 Madrid, Spain

ABSTRACT

Fiber cement industry is well-known for its efforts to reduce the environmental impact which has allowed a high process water recycling and a minimization of the use of fresh water. However closed water circuits promote the accumulation of contaminants in the process water which may affect the process and the product quality. Whitin the contaminants, hexavalent chromium accumulation is a challenge since it increases the final content of leachable and toxic hexavalent chromium in the final product. Therefore, new solutions in this field are needed to prevent that the water circuit closure affect the environmental impact of the final product.

To minimize the chromium concentration in process water of closed water circuits, a kidney treatment based on an adsorption process is proposed. This kidney treatment consists of an intermediate treatment of a certain flowrate of the process water is partially to remove the excess of a certain contaminant, avoiding its buildup in the process. Thus, in this case, the hexavalent chromium would be adsorbed before water reuse in the production process, preventing from overconcentration in the process water recycling. In this work, different adsorbents have been tested with process waters, being the most efficient ones granular and powdered commercial activated carbons as well as a novel advanced adsorbent based on nanocellulose material.

Results show that all adsorbents remove more than 99% of hexavalent chromium from complex fiber cement process water under optimized conditions. The novel nanocellulose based adsorbent has shown the best results. The operation and mechanisms associated to the application of this advanced adsorbent are completely different from those of activated carbons. Each adsorbent shows varied requirements which need to be assessed and optimized before its industrial implementation. Optimal operation conditions for each material involve modifications in the process which have been analyzed and tested to obtain a clear comparison of the different adsorption alternatives from a technical and economic point of view.

Therefore, this presentation includes a comparative analysis of the costs of different process water alternative treatments for chromium removal. Results will facilitate the decision-making of the final industrial user when chromium contamination must be managed in the process.

KEYWORDS:

Nanocellulose, activated carbon, adsorption, hexavalent chromium, fiber cement process.

INTRODUCTION

Water availability and water quality are key challenges in fiber cement production by means of the Hatschek process. Water is used for fibres and minerals dispersion and transport throughout manufacturing but water is also required for cement hardening, which affect the final product quality. Around 0.24 m^3 of process water are involved per each square meter of fiber cement product. Most of the process water is recovered and reused in the process, reducing the demand of freshwater notably. Fibre cement industries have already carried out a great effort in water recycling processes to reduce freshwater consumption down to the recovery of evaporated water during Hatschek process. These closed water circuits suffer from the accumulation of organic and inorganic contaminants which has a strong effect on the process runnability and on the final product quality. The presence of a large amount of organic matter can affect the quality of fibre cement sheets and a high content of metals such as hexavalent chromium leads to a final release of this contaminant to the environment with the wastewater disposal but it also affects the quality of the final product.

Hexavalent chromium comes mainly from cement, especially when the cement used as raw material contains fly ashes from waste incineration plants. Part of the hexavalent chromium in these cements is lixiviated in the process water and concentrated cycle by cycle, reaching concentrations near the regulated limit for the wastewater. Furthermore, the high concentration of hexavalent chromium in the process water can increase the final content of leachable and toxic hexavalent chromium in the final product. The amount of discharged wastewater is small, but it must be treated before discharging it and the presence of hexavalent chromium difficulties this treatment.

To avoid the accumulation of pollutants, a kidney intermediate treatment can be used in the process water aimed to remove hexavalent chromium. The most appropriate treatment is a kidney process based on the adsorption of pollutants from water onto a suitable adsorbent, such as activated carbon (Pakade et al, 2019; Ukhurebor et al, 2021). Previous works have tested different adsorbents with process waters, being the most efficient ones the granular and powdered activated carbons and the novel advanced nanocellulosic materials. The last have shown the best results for hexavalent chromium removal.

The adsorption on activated carbon requires using at least two parallel fixed beds: one working and the other being regenerated with clean water. The regeneration of the adsorbent consumes water and produces a stream with a higher concentration of hexavalent chromium to be managed. This stream can be treated by means of reverse osmosis to concentrate the pollutants and recover up to the 85% of the water. This generates a highly concentrate wastewater that can be managed by a waste gestor external to the company or by evaporation to recover more water and further concentrate the hexavalent chromium in the minimal volume to reduce the management costs and the environmental impact.

A novel adsorbent, based on hairy cellulose nanocrystals (CNC) has been recently proposed and tested in a previous research. This adsorbent is a kind of nanocellulose having two positively charged amorphous ends joint through a common crystalline shaft (Campano et al, 2019; Yang et al, 2016). It is produced by means of three steps (Yang et al, 2013):

- Firstly, cellulose is oxidated by $NaIO_4$. This oxidation transforms the C2-C3 hydroxyl groups of the glucose units into aldehydes, while simultaneously breaks the C2-C3 bond.
- Secondly, the aldehyde groups are easily modified, for example through a Schiff base reaction that introduces quaternary ammonium groups creating cationic sites. Different modifications can be made to give specific properties and charge to the hairy nanocellulose.
- Finally, the modified fibers are fallen apart in nanocrystalline cellulose with modified amorphous regions attached to both ends by means of a thermal treatment, while the remaining amorphous regions is solubilized.

Hairy CNC are highly biodegradable and have shown great properties to enhance the adsorption of a wide variety of contaminants. They have been proved in different applications, but mostly for dye removal (Tavakolian et al., 2019; Bassyouniet al, 2022). Huang et al, (2020) demonstrated that hairy CNC were also efficient for the removal of hexavalent chromium from pure dichromate solutions. However, this method has not been validated yet with real industrial process waters. Previous works carried out in the IIBCC project titled “Fiber cement industry: Water management and treatment for an environmental friendly closed circuit manufacture” have proved that hairy nanocrystals are able to remove the 100% of hexavalent chromium and furthermore that this contaminant can even be changed to trivalent chromium, which is a micronutrient.

Hairy CNC cannot be regenerated as in the case of active carbon. However, they can be incorporated into the product acting also as a reinforced agent which maybe an additional advantage. Although they are not commercial products nowadays, they show a great potential. In this work they are compared with other suitable commercial removal systems from the economic point of view to analyse the real potential of CNC and the economical limits for their future price. The comparison requires analysing the operating conditions and the adsorption efficiency of each material to determine the optimum adsorbent amount for the optimum hexavalent chromium removal and to evaluate the implementation of the treatment within the current process water circuits.

Therefore, the objective of this paper is to determine the maximum costs of hairy CNC per ton that make economically feasible its use as adsorbent in comparison to the implementation and operation costs of a traditional intermediate process based on activated carbon for real industrial waters sampled from different hatcheck processes.

MATERIALS AND METHODS

Different adsorption processes were evaluated for process water from three different fiber cement production plants with a hexavalent chromium concentration varying from 3.5 to 6.5 mg/L.

Selection of adsorbents

The applied granular and powdered activated carbon (GAC and PAC) for these adsorption tests were previously selected between different commercial activated carbons. The maximum hexavalent chromium removal was found by using CG900 and CP8 activated carbons, purchased from Chiemivall, Spain. These materials were chosen to perform this study. The hairy CNC were produced at lab scale, following the protocol indicated at the introduction part.

Batch adsorption tests

Batch adsorption tests up to equilibrium were developed. A multireax device (Heidolph, Germany) with a total stirring capacity of 12 samples (50 mL/sample) was used. The use of this device allowed the full optimization of dosage of each material to the treatment of each industrial process water in just one adsorption batch test. To perform the test, a certain amount of adsorbent was added to each water sample in Falcon tubes and then, they were kept stirring for three hours. Once finished, samples were filtered through 0.45 microns syringe filter to measure hexavalent chromium through a UV-Vis spectrophotometer following Standard Method 3500 Cr B (APHA, 1992).

Technical-economic assessment of activated carbon and hairy CNC adsorption processes

This study is focused on the technical-economic comparison of two wastewater treatment adsorption processes, the conventional process through activated carbon column adsorption and the novel process through hairy CNC addition. Both processes require a pH adjustment to enhance the final performance of the adsorption treatments. The designed process will be considered as a kidney treatment, which receives only a part of the total process water, large enough to reduce the hexavalent chromium content to prevent overconcentration above a fixed limit.

<u>Conventional process:</u>

The conventional process involves the use of two granular activated carbon columns in parallel for a continuous treatment of the process water to remove the hexavalent chromium. GAC columns must be washed with fresh water (with an equivalent volume of 10% of treated water volume) between cycles. Washing water is highly concentrated in hexavalent chromium and other pollutants from the process water. The implementation of ultrafiltration (UF) and reverse osmosis (RO) membranes, recovering 85% of treated water, allows its reuse in the process. The 15% of reject from the membranes as well as the washing water used to clean the membranes requires a new recovery treatment based on evaporative technologies. This process allows the recovery of 85% of water as high-quality steam which can be easily used in different parts of the fiber cement production process and minimizes the volume of hexavalent chromium-concentrated waste management, a key factor for economic feasibility of the process.

<u>Novel adsorption process:</u>

The implementation of hairy CNC as adsorbent is easy and efficient. This material is added directly to the process water into a stirred tank. There, hairy CNC adsorbs hexavalent chromium and rapidly reduces it into less toxic trivalent chromium. Process water can be directly sent to the process without any posterior treatment since CNC may act as reinforcement agent without affecting negatively the process neither the product (Balea et al, 2019).

Considerations for technical-economic assessment

Average energy and chemicals consumption of UF and RO membrane and evaporation treatments were taken from bibliographic references (Perez et al, 2022; Mugaishudeen et al, 2013; APV, 2008; Vondra et al, 2017). Heat savings through steam recovery were estimated as natural gas equivalent heating energy.

Capital costs of GAC columns, UF, RO and evaporation were estimated from bibliography (Guo et al, 2014; Samco, 2017; APV, 2008). Energy costs were estimated according to the evolution of non-household energy prices in the EU shown by the official website Eurostat (Eurostat, 2022). The evolution of natural gas prices for heat saving estimation was also found in Eurostat. Waste management costs were obtained by the official tax of public management of hazardous waste in Spain (Government of Aragon, 2022). Chemicals costs were achieved from the study of Perez et al (2022).

RESULTS

Optimal GAC dosage

The optimization of GAC dosage was carried out through a cost-efficient non-linear estimation and this value was compared with the typical linear estimation. These optimal values correspond to the dosages where the curves (grey for non-linear cost-efficient estimation and blue for linear estimation) cross 100% of hexavalent chromium removal. The results obtained for one of the tested process waters can be seen in figure 1. Similar trends were seen in the rest of the treated waters.

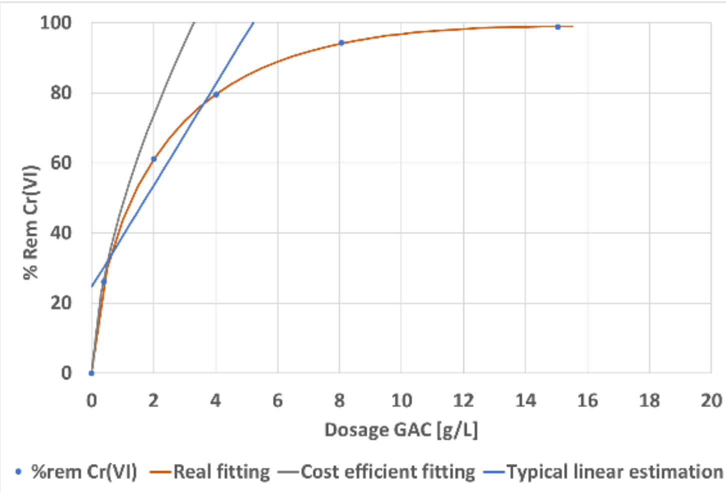


Figure 1. Hexavalent chromium removal efficiency under varied GAC dosages treating process waters from Process plant 1 (PP1) (dashes), real fitting (orange line) cost-efficient estimation (grey line) and linear estimation (blue line)

There is a saturation trend in the adsorption efficiency with dosage, which can be perfectly estimated (orange curve). A variable optimal dosage depending on the process water quality was found. While process water from PP1 (figure 1) and PP2 could be treated under 3.30 and 3.01 g/L of GAC, PP3 only needed 1.03 g/L of GAC dosage as optimal. The use of non-linear estimated dosage for the evaluated cases shows a reduction of 35-55% compared to the linear estimation, which can be critical for the final implementation of GAC columns.

Optimal PAC dosage

The evolution of hexavalent chromium adsorption with PAC dosage was also evaluated. In this case, the linear estimation was accurate to predict the most efficient adsorbent dosage due to the sharp growth of the curve. The obtained curves of treatment of PP1 process water with varied PAC dosages can be seen in figure 2.

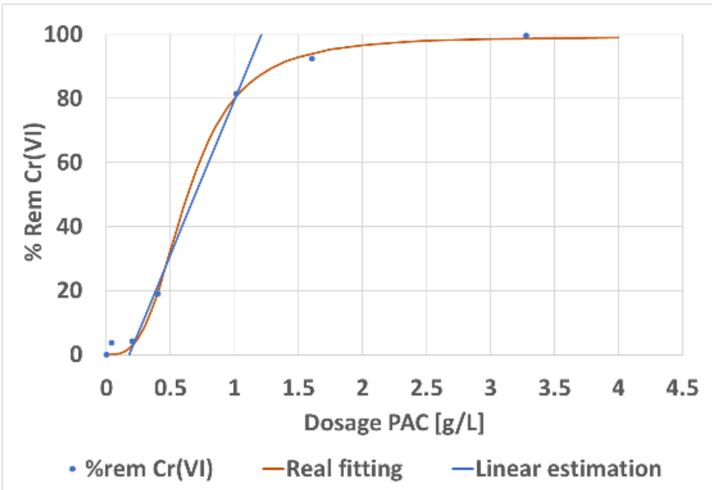


Figure 2. Hexavalent chromium removal efficiency under varied PAC dosages treating process waters from Process plant 1 (PP1) (dashes), real fitting (orange line) cost-efficient estimation (grey line) and linear estimation (blue line)

The sharp trend of chromium removal with PAC dosage can be found in all the tested process waters. This fact indicates the need of a minimal PAC dosage to reach high removal, instead of a smooth increase of efficiency with adsorbent mass. In general terms, the dosages of PAC were lower than those of GAC. That could be expected from the higher exposed surface (lower particle size). PP1 process water needed 1.20 g/L (figure 2) as optimal dosage while PP2 and PP3 process waters show good adsorption yields under 0.70 g/L.

Optimal hairy CNC dosage

Hairy CNC dosage effect in hexavalent chromium removal was also tested. In this case, the adsorbent was dosed in 1% (w/w) suspensions and the value of dosage corresponds to solid mass of adsorbent per process water volume. The resulting fittings of hexavalent chromium removal with hairy CNC dosage for PP1 process water is plotted in figure 3. According to the resulting curves shown in figure 3, the optimal adsorbent dosage to remove hexavalent chromium for PP1 was 0.14 g/L of hairy CNC dosage (figure 3). The optimal estimated values obtained in the case of PP2 and PP3 were 0.25 and 0.06 g/L, respectively. The wide spread of dosages remarks the relevance of analysing the treatment of each water individually and design each treatment as a turnkey project. The obtained optimal dosages show a reduction in 1-2 orders of magnitude in contrast with PAC and GAC, respectively.

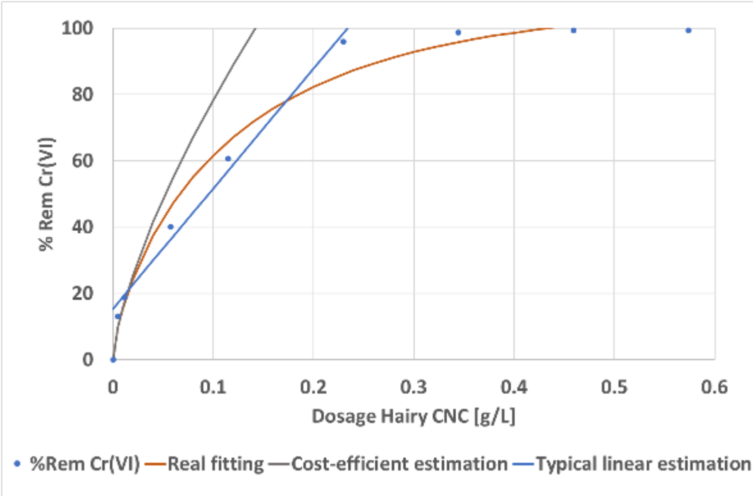


Figure 3. Hexavalent chromium removal efficiency under varied hairy CNC dosages treating process waters from Process plant 1 (PP1) (dashes), real fitting (orange line) cost-efficient estimation (grey line) and linear estimation (blue line)

Cost estimation of GAC column adsorption treatment

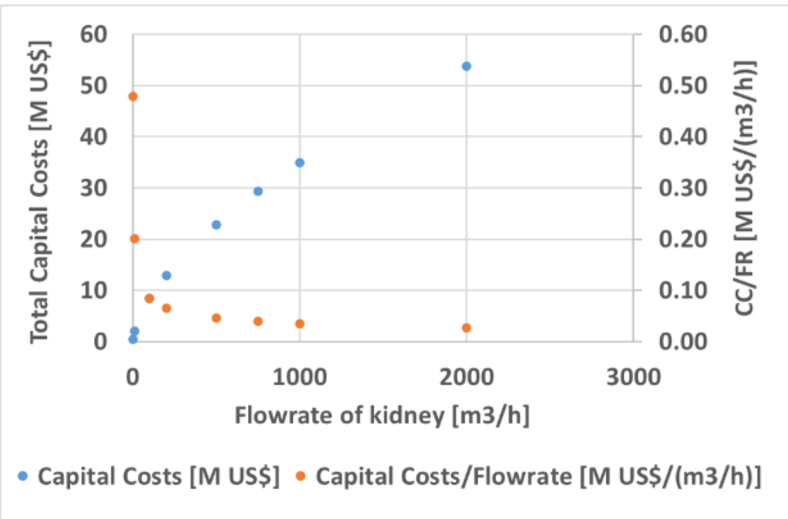
Once the GAC dosage was optimized, the cost analysis of using GAC columns could be performed applying the previously mentioned considerations. The cost evaluation will be divided in the capital costs and the operation and maintenance costs estimations.

Capital costs estimation

The capital cost estimation includes the implementation of the following equipment to treat the process water in the kidney treatment process and the mentioned derived flowrates of washing water, as well as the inlet design flowrate:

- GAC adsorption column: 100% of kidney treatment process flowrate
- UF and RO membranes: 8-10% of kidney treatment process flowrate
- Wastewater evaporator: 2.5% of kidney treatment process flowrate

The evolution of total capital cost estimation (blue dots) and capital cost per unit of flowrate (orange dots) with the kidney treatment process flowrate, as well as the distribution of the costs between treatments can be seen in figures 4 a, b.



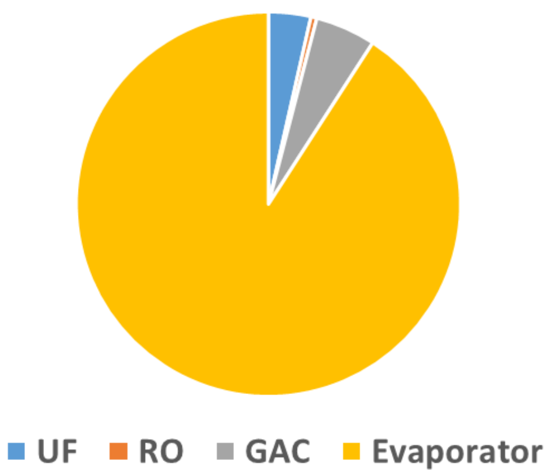
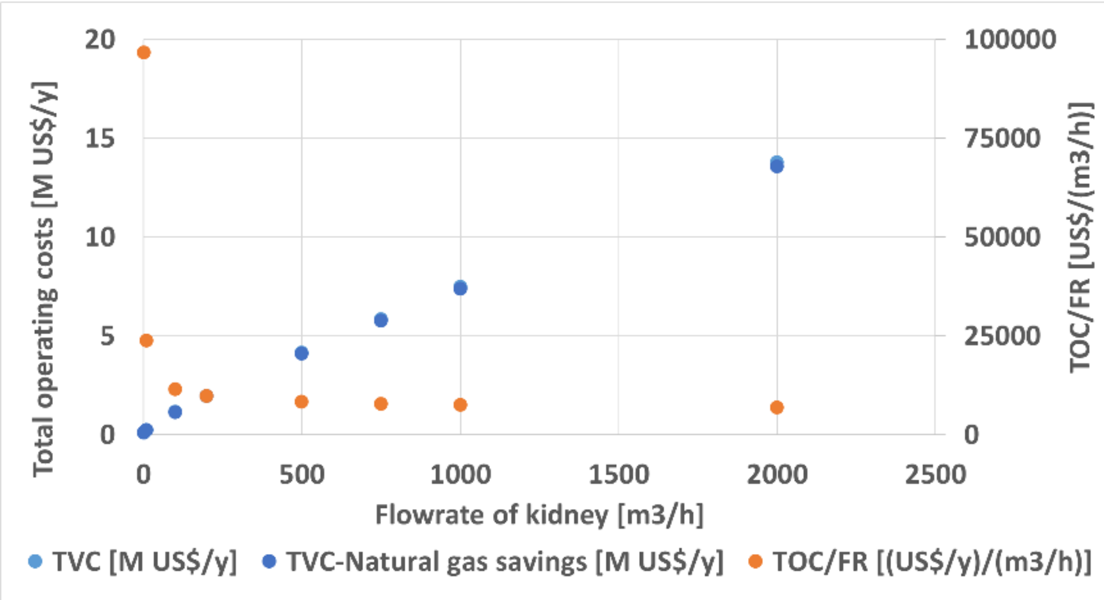


Figure 4. a) Evolution of total capital costs [M US$] (blue dots, left axis) and capital costs per unit of flowrate [M US$/($m^3$/h)] (orange dots, right axis) and b) Distribution of capital costs between treatments.

The curves obtained in figure 4a show a logical continuous increase of capital costs (blue dots) with flowrate but in terms of economy of scale, the unitary costs (per m^3/h of kidney treatment process flowrate) decreased to get a stable value at a flow rate around 200 m^3/h, meaning that the process would be economic efficient for similar and higher flowrates.

Variable cost estimation

The operation variable costs were also estimated for the GAC adsorption treatment under different classifications: waste management, energy, GAC purchase, chemicals, maintenance, and others. The result for the different kidney treatment process flowrates and the distribution of costs are shown below in figure 5.



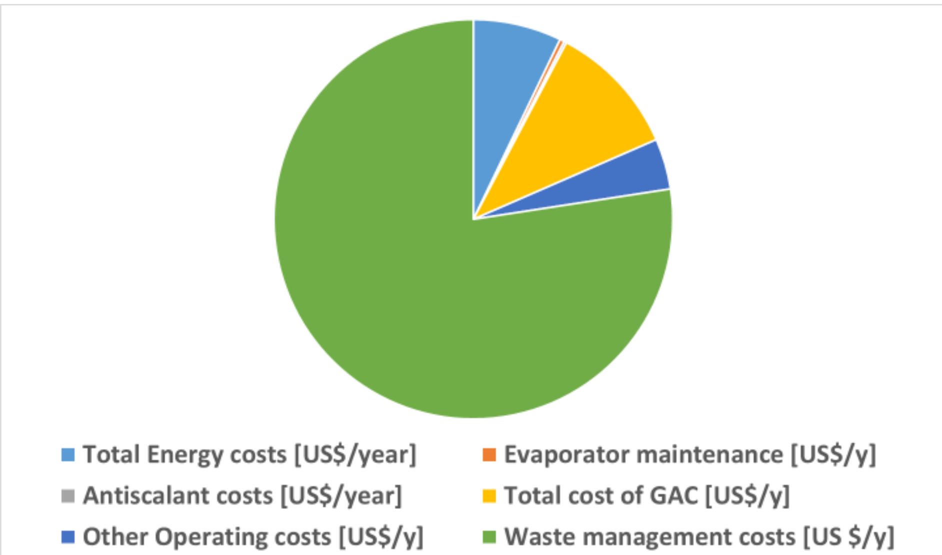


Figure 5. a) Evolution of total variable costs [M US$/y] (blue dots, left axis) and capital costs per unit of flowrate [(M US$/y)/($m^3$/h)] (orange dots, right axis) and b) Distribution of variable costs between treatments.

The dependence of variable costs with flow rate (figure 5a) is like that for the capital costs (figure 4a), reaching economy of scale with kidney treatment process flowrates upper than 100 m^3/h. More than 75% of the variable costs are due to the management of the waste leaving the evaporator at the final stage (figure 5b). This value is remarkably high due to the expensive taxes of hazardous waste in European countries. Compared to this factor, energy and GAC costs do not even reach 20% of the overall O&M costs together. The high impact of the waste management cost shows the need of sustainable processes with minimal or zero waste generation to prevent the process from associated environmental impact and excessive costs.

Cost estimation after replacement of evaporation technology with a second membrane process (UF and RO)

The cost analysis was also performed to evaluate a variation in the process by implementing a second unit of membrane treatment combining UF and RO to concentrate the reject effluent from the first treatment of washing water. The results of cost comparison under 10 m^3/h of kidney treatment process flowrate can be seen in figure 6.

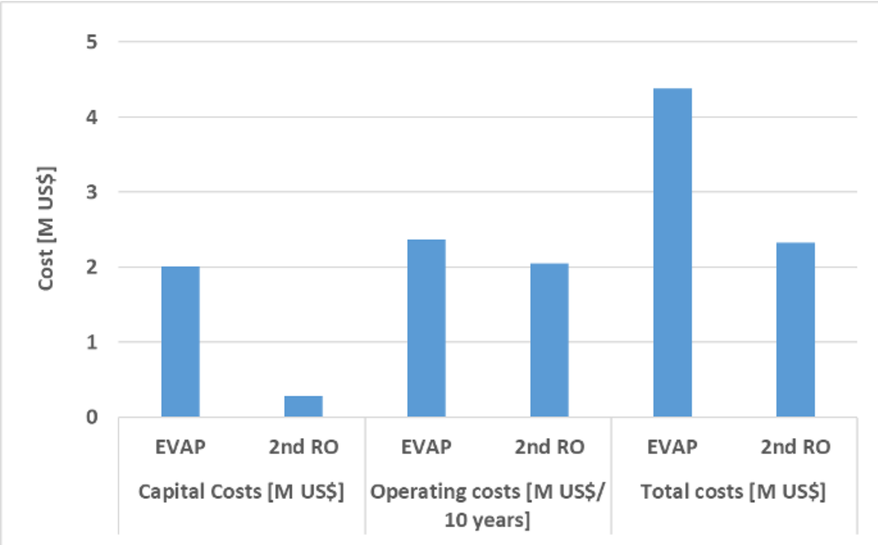


Figure 6. Capital, operating and total cost comparison of 10 m^3/h of kidney treatment process flowrate by implementing an evaporator (EVAP) or a second membrane treatment (2nd RO) to concentrate the first reverse osmosis reject

The costs shown in figure 6 reveal a critical reduction of capital costs of 86%, as the purchase of the evaporator is much expensive than the equivalent membrane system, as this device is commonly composed of stainless steel with a remarkable thickness, compared to low-cost membranes. The operating costs of both processes are similar, as the flowrate of generated waste is similar, and the maintenance costs of the evaporator are comparable to the periodic substitution of membranes. The reduction of operating costs is mainly caused by the 90% reduction of energy costs associated to the use of membranes. Overall, the total estimated costs of installing a second membrane unit were 46% lower than the evaporation technology, which enhances the implementation.

Cost estimation of hairy CNC for economic feasibility of implementation

The cost estimation of hairy CNC addition depends on the production plant, as each production plant shows different characteristics: water quality, kidney treatment process flowrate, etc. which modifies the result of needed adsorbent dosage and the capital and variable costs of the conventional treatment. The defined maximum hairy CNC implementation cost is defined as the top value of this material in the market which makes the implementation of hairy CNC adsorption a cost-effective treatment compared to the implementation of conventional treatment. Whenever the market value of this novel nanocellulosic material goes down below the mentioned value, the overall cost of the process can be comparable to the use of activated carbon. Figure 7 shows the evolution of the hairy CNC implementation cost with the intermediate treatment process flowrate.

Figure 7 indicates that in the case of large kidney treatment process flowrates (higher than 100 m^3/h), the cost of hairy CNC must be lower than 20 US$/kg to be cost comparative to the conventional activated carbon. In the case of low flowrates, this cost depends on the kidney treatment process flowrate and has a top value of 100 US$/kg when the kidney treatment process is 1 m^3/h. In this case, which can be adequate for small industrial facilities or even pilot plants, the implementation of hairy CNC requires an inexpensive amount of money in contrast to a more complex treatment composed of three steps like the conventional one. Soon, these costs of implementation are expected to be increased due to the present rise of energy costs and hazardous waste management affecting the operation costs of kidney treatment process.

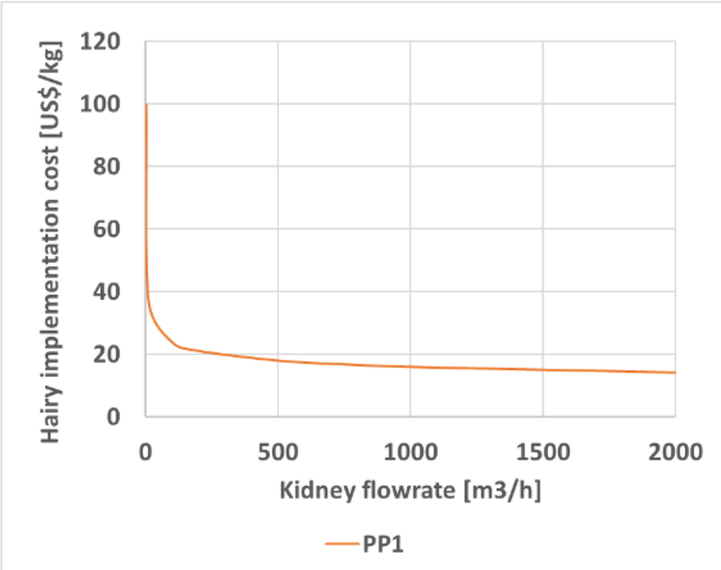


Figure 7. Hairy CNC [US$/kg] maximum implementation cost under varied kidney treatment process flowrates in PP1

CONCLUSION

The cost estimation of water process treatment to prevent hexavalent chromium contamination in fiber cement production is a key factor to determine the process technical and economic feasibility. The application of conventional granular activated carbon (GAC) and powdered activated carbon (PAC) and novel hairy cellulose nanocrystals (CNC) adsorbents in process waters from three industrial facilities was analysed. The average cost-efficient dosage for GAC, PAC and hairy CNC were 2.45, 0.87 and 0.15 g/L, respectively. The cost analysis of GAC column as kidney treatment process treatment for hexavalent chromium combined with membrane treatment (ultrafiltration and reverse osmosis) to treat washing water and evaporation to treat the membrane reject was performed. The economy of scale of the process was reached when the kidney treatment process flowrate overpassed 100 m^3/h with a total cost of 0.10 M US$/($m^3$/h). Most of the capital (>90%) and variable costs (>75%) were associated to the evaporator and waste management, respectively. The cost-estimation when evaporation was substituted by a second membrane process revealed a 46% of total costs reduction, caused by a 90% of reduction of capital costs when purchasing membranes instead of the wastewater evaporator. The implementation cost of hairy CNC was analysed compared to the conventional process, showing that the value of this material to reach a cost-efficient treatment process must be below 20 US$/kg for large kidney treatment process treatments (over 100 m^3/h) or below 100 US$/kg for small facilities and pilot plants. These results indicate a promising impact of nanocellulosic materials in the sustainable water management in fiber cement production plants.

ACKNOWLEDGMENTS

The authors wish to thank the IIBCC Committee for funding this research, the Community of Madrid and the Economy and Competitiveness Ministry of Spain for their support to projects S2018/EMT-4459 (RETO-PROSOST-CM) and CTQ2017-85654-C2-2-R, as well as the support of the Economy and Competitiveness Ministry of Spain for the grant provided to F.B. Ojembarrena (PRE2018-085034).

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