Innovative Treatment of Combined Sewer Overflow and perspective of Hydrochar reuse for pollutants adsorption

Alice Botturi [a*]; Nicola Frison [a]; Chiara Giosuè [b]; Anna Laura Eusebi [b]; Fabio Merzari [c]; Luca Fiori [c]; Francesco Fatone [b]

a. University of Verona, Department of Biotechnology, Strada le Grazie 15, 37134 Verona, Italy
b. Polytechnic University of Marche, Department of Materials, Enivironmental Sciences and Urban Planning SIMAU, Piazza Roma, 22, 60121 Ancona, Italy
c. University of Trento, Department of Civil, Environmental and Mechanical Engineering, via Mesiano 77, 38123 Trento, Italy

* Corresponding author:
E-mail address: alice.botturi@univr.it

ABSTRACT

The Combined Sewer Overflows (CSOs) are one of the main problems which affected the area provided with a Combined Sewer System (CSS). The impact of the discharge of the untreated wastewater (CSOs) into water basin is a serious problem for local flora and fauna. The best treatments to treat these overflows are under study. The project is focused on analysis of innovative treatments to be applied in the area of Garda Lake, specifically in Lazise (Verona, Italy). In this work, it was studied the adsorption treatment in order to evaluate the performance in terms of the removal of organic matter and of metals. In detail, two adsorption materials were analyzed: a commercial one and an experimental one. Four commercial Granular Activated Carbons (GACs) were analyzed and the behavior of hydrochar (HC) produced from hydrothermal carbonization (HTC) at two different temperature (190° and 250°) was tested. The results show the two best commercial GAC that were used to design the activated carbon unit in the demonstrative site located in Lazise for the CSO treatment. Concerning the hydrochar, the best results were obtained with lower HC concentrations (0.5 g/L).

KEYWORDS

Combined sewer overflow, CSO, Innovative Treatment, Hydrochar, HC, Granular Activate Carbon, GAC

ABBREVIATIONS

CSO	Combined Sewer Overflow
CSS	Combined Sewer System
EDS	Energy Dispersive Spectroscopy
GAC	Granular Activated Carbon

HC	Hydrochar
HTC	Hydrothermal Carbonization
sCOD	Soluble COD
SEM	Scanning Electron Microscope
UWWTD	Urban Waste Water Treatment Directive
WFD	Water Framework Directive
WWTP	Wastewater Treatment Plant

INTRODUCTION

Combine sewer system (CSS) is a typical infrastructure designed to collect rainwater runoff, domestic wastewater and industrial wastewater into the same pipeline. Normally, the CSS transports all the wastewater to a wastewater treatment plant (WWTP). However, during intense rain events, the capacity of the CSS may be exceeded, causing the discharge of untreated wastewater directly to nearby streams, rivers or other water bodies. These overflows, named Combined Sewer Overflows (CSOs), are consequently diluted streams, mainly characterized from sources of microbial pathogens, contaminants, chemicals, suspended solids, heavy metals and nutrients. The Urban Waste Water Treatment Directive (UWWTD) recognizes that, although the CSO flow is diluted by significant amounts of rainwater, it can affect negatively the environment. Since the start up of environmental legislation in Europe in the 1970's, attention has been paid to the impact of CSO on the receiving water quality. The Water Framework Directive (WFD), adopted in 2000, has further motivated CSO monitoring campaigns in all European countries with the aim to study the pollution discharge to the receiving waters. The WFD recognized that the Europe's water is under pressure with about 20% of surface water is at serious risk from pollution. EurEau [1] estimate that across Europe there are about 650.000 CSOs and their impact on the receiving water body is an issue of increasing concern because it may lead to restrictions in the use of the receiving waters. Currently, the main techniques applied for the treatment of CSOs before the final discharge are based on preliminary treatment, such us sand and/or grit removal. The physical units are obviously not sufficient for the decrease of all the pollutants and microbiological loads in the CSOs. Therefore, to date, different treatments are studying in Europe and in USA, as possible solutions to this problem. Most of the studies are focused both on technological options (chemical disinfection, adsorption) [2, 3] and on natural treatments such as constructed wetland [4]. The activities of this paper is inserted in the framework of the Intcatch2020 project (Horizon 2020, GA 689341) where an innovative process based on sieving and activated carbon/UV was applied in the demonstrative site of Villa Bagatta (Verona, Italy) for the treatment of CSOs discharge into the Garda Lake. In this work, preliminary tests were carried out with real

CSOs for the adsorption of soluble COD (sCOD) and of the main metals. The adsorption process was applied by using both conventional matrix (Granular Activated Carbon, GAC) and hydrochar (HC) from sewage sludge without activation, an innovative media derived from the hydrothermal carbonization (HTC) process [5, 6]. In the literature, activated hydrochar has recently received increased attention as low cost potential adsorbent for contaminant removal [7]. On the other side, no many information about the HC behavior in not-activated forms is available.

MATERIALS AND METHODS

HC production

The HC was produced in a HTC stainless steel batch reactor designed and constructed in-house at the University of Trento. The HTC reactor has an internal volume of 2 L and is designed for maximum temperature and pressure of 300 °C and 140 bar, respectively. For this research, two kinds of HC were tested, produced respectively at 190 °C and 250 °C with one hour of residence time at the set point temperature.

The feedstock used to produce HC was digested sludge, both raw and dewatered. Digested-dewatered sludge (23.3% dry matter) was diluted with digested sludge (1.2% dry matter) in order to completely submerge the former with the latter, as HTC has to occur in a liquid water reaction environment. Both kinds of sludge were sampled from the sludge line of “Trento North” WWTP, Italy: digested sludge just after the anaerobic digester, digested-dewatered sludge after the centrifuge.

For each experiment, the reactor was charged with 400 g of digested-dewatered sludge and 350 g of digested sludge, and thus the dry mass to water ratio was equal to 0.15. The reactor filling degree was about 50%, due to the low density of digested-dewatered sludge. Even if in previous works we used a smaller HTC reactor, actually the experimental procedures used to produce HC and, in the following, to dry it and evaluate the HC yield were maintained the same [8, 9].

For the 2 L HTC reactor, about 40 minutes were necessary both to reach the set point temperature and to cool down the system after the residence time at the HTC set point temperature was passed.

Preliminary characterization of GAC and not-activated HC

The major aim of the batch tests was to investigate the capability of three different commercial GACs to adsorb pollutants. The commercial GACs are ST300, STW400, ST100 and were provided by Carboplant srl (Vigevano, Italy). The preliminary batch results were used to choose the carbon to be applied in the demonstrative site of Villa Bagatta.

Moreover, the possible use of not-activated HC as an adsorbent media has been verified. Specifically, the tested HC was used as *raw HC* and as *washed HC*, after three hours of contact time in distilled water.

The surface morphological structure and the ash chemical composition of the commercial GACs and of both not-activated HCs were analyzed by Scanning Electron Microscopy (SEM) coupled to Energy Dispersive Spectroscopy (EDS) (Philips XL20). The samples were mounted on a stub of metal with adhesive, then they were coated with Gold and then observed in the microscope. The pH of the HC was measured using a pH meter (Medidor PH Basic20) after the addition of 1 g of HC in 20 ml of distilled water and mixed for 3 hours. The technical characteristics of the commercial GAC were reported in Table 1. Although the main differences were linked to the different porosity (8X30 and 12X40), also the size particle distributions of each GAC type were analyzed using a series of sieves (USA ASTM) and following the standard method ASTM 689341.

NAME	**ST 300**	**ST 300**	**STW 400**	**STW 400**	**ST 100**
TYPE	Mineral GAC	Mineral GAC	Mineral GAC	Mineral GAC	Mineral GAC
SIZE DISTRIBUTION [U.S. mesh]	8x30	12x40	8x30	12x40	8x30
DENSITY [g/L]	500±20	500±20	500±20	500±20	520±20
UMIDITY [%]	<2	<2	<2	<2	<2
IODINE NUMBER [mg/L]	>950	>950	>1000	>1000	>750
METHYLENE BLUE INDEX [mg/L]	>180	>180	>190	>190	>150
ABRASION NUMBER [%]	> 80	> 80	> 80	> 80	> 80
HARDNESS [%]	> 90	> 90	> 90	> 90	> 90
ASH LEVEL [%]	< 15	< 15	< 15	< 15	< 15
SURFACE AREA [m^2/g]	> 950	> 950	> 1000	> 1000	> 800

Table 1 Characterization of the commercial GAC

Batch adsorption experiments for GAC and not-activated HC

The adsorption experiments were carried out at constant temperature (23 ± 2 °C), under stirring and different concentrations of GAC and not-activated HC.

The GAC batch test consisted in a volume of 0.8 L of CSO (with a sCOD concentration of about 30 mg sCOD/L) and four different concentrations were evaluated: 2 g/L, 5 g/L, 10 g/L, 20 g/L.

The not-activated HC was washed with 0.8 L of distilled water at two different concentrations (0.5 g/L and 5 g/L) in order to evaluate the potential release of sCOD, according to [10] (Test 0_A_HC). Then a second test was performed (Test 0_B_HC) in order to verify the behavior of the washed HC. The same concentrations of not-activated washed HC were put in contact with two different wastewaters, characterized respectively by about 200 and about 30 mg sCOD/L in order to simulate different sCOD concentrations (Test 1_HC and Test 2_HC). The concentration of 30 mg/l of sCOD (and a concentration of 60 mg COD/L) was representative of diluted values of ordinary CSO. During the batch test, the samplings were performed at different time for 3 hours.

The same procedure was adopted to study the adsorption capacity at different concentrations of metals (Test 3_HC), chosen in order to reproduce the characteristic pollution presence in a real CSO. The samples were immediately filtered at 0.45 µm and analyzed to determine the main parameters according to the Standard Procedure [11].

The adsorption capacity of the GAC was described according to the Freundlich isotherm expressed by the following equation:

$$\frac{x}{m} = \frac{abCe}{1+aCe}$$

Where x is the mass of the adsorbate; m is the mass of the adsorbent; x/m is the adsorption capacity of the carbon; a and b are empiric constants; C_e is the final equilibrium concentration of the pollutants in the liquid phase.

RESULTS AND DISCUSSION

HC yield

As well-known from literature, the higher the HTC temperature, the lower the hydrochar yield [12, 13]. In the present case, the HC yield (expressed as the ratio of the mass of the HC and the mass of the feedstock used to produce it, both on a dry basis) resulted equal to 0.85 and 0.67 for the HTC performed at 190 and 250 °C, respectively.

Surface and elemental composition of GAC and HC

The results obtained from size distribution analysis of GAC, were used in order to make particle-size distribution curves. As shown in Table 2, the coefficient of uniformity (Cu) is <2 for each GAC type, testifying that the carbon is quite uniform.

GAC type	**C_u**
ST100 8X30	1.4
ST300 8X30	1.5
ST300 12X40	1.6
STW400 8X30	1.5
STW400 12X40	1.7

Table 2 GAC coefficient of uniformity

The Fig. 1 shows the pictures made by SEM for each carbon type. Also from the microscope analysis, the average activated surfaces of the commercial GACs ranged between 1-2 mm.

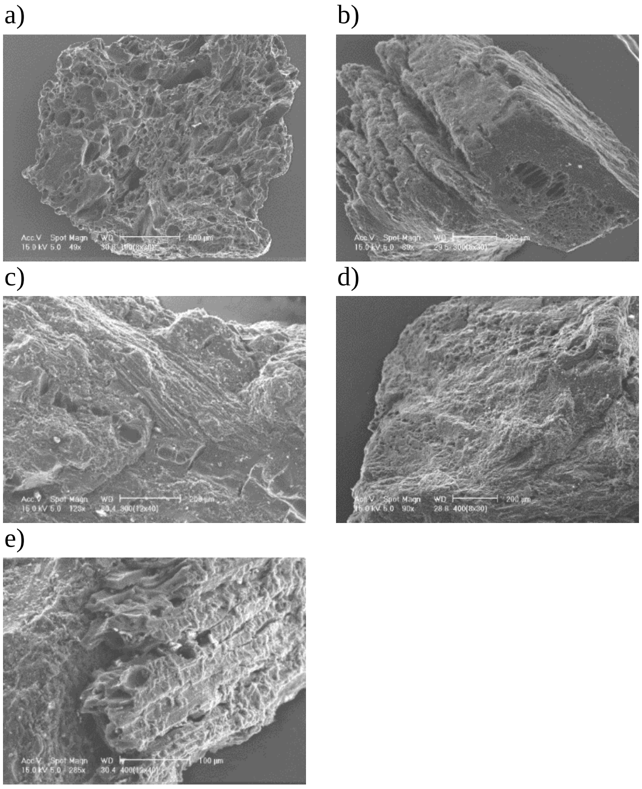

Figure 1 SEM analysis GAC ST100 8x30, 50X (a); GAC ST300 8x30, 70X (b); GAC ST300 12x40, 120X (c); GAC STW400 8x30, 90X (d); GAC STW400 12x40, 270X (e)

The not-activated HC, produced at 190 °C and 250 °C (in what follows referred to as HC190° and HC250°), was analyzed as *raw* and *washed HC*. The performed analysis has given insight on the physical and chemical properties of the HC. The results of the metals content are summarized in the following table (Table 3). The raw HC190° has a different elemental composition if compared with HC250°. Indeed the HC250° does not show the presence of Zn, Mn and Na. Moreover, the SEM analysis showed the average granulometric distribution for the not-activated HC (Fig. 2). As it is showed in the pictures, the average dimension of the HC is in the range 50-500 µm.

	EDS microanalysis (wt%)									
	Zn	Mn	Na	Al	Si	P	S	K	Ca	Fe
Raw HC190°	1.2	0.9	3.7	7.5	6.6	18.1	8.2	1.1	17.6	31.4
Raw HC250°	-	-	-	8.6	7.4	20.7	7.9	0.9	20.4	31.0
Washed HC190°	0.9	0.6	3.9	9.6	8.8	21.3	7.1	0.9	17.9	24.3
Washed HC250°	-	-	-	10.2	8.7	23.5	8.2	0.8	19.1	25.8

Table 3 Microanalysis of raw and washed HC obtained at 190° and 250°

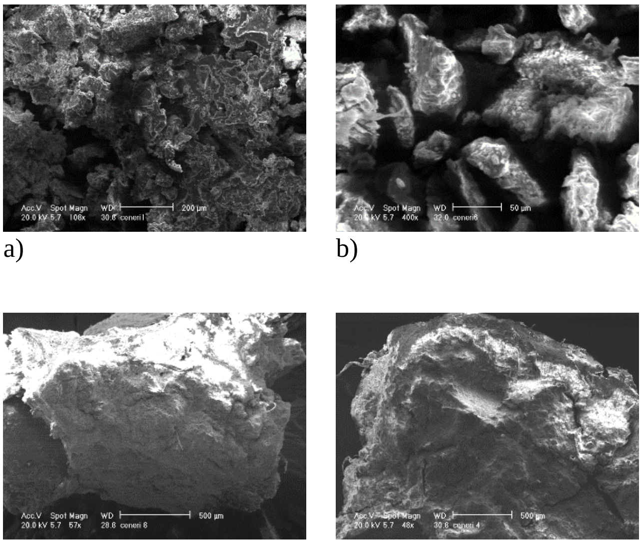
a) b) c) d)

Figure 2 SEM analysis HC250° (a 100X, b 400X); HC190° (c 70X, d 50X)

GAC batch experiments

The Figure 3 shows the percentage of removal efficiency (E%) of all carbons tested. It can be noted that for low doses (2 and 5 g/L), the carbons STW400 8X30, ST300 12X40 and ST100 8X30 show a removal efficiency of about 50% up to a maximum of 80% at high doses (10 and 20 g/L). An increase of about 70% for the carbon ST300 8X30 is shown with maximum percentage of abatement of about 85% for a dosage of 10 g/L. Similarly, the carbon STW400 12x40 has the same removal capacity for both 10 g/L and 20 g/L, while for low dose it is not very efficient. Furthermore, it is evident the linear proportionality between the dosages and the removal percentages for the carbons ST100 8X30 and STW400 8X30, until the carbon concentration of 20 g/L.

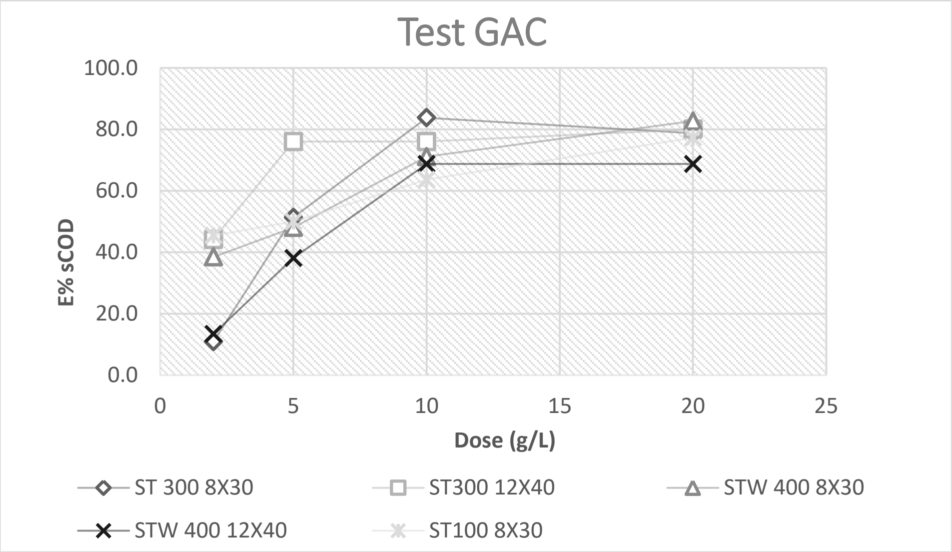

Figure 3 Summary of E% sCOD for GAC test

The adsorption ability for each carbon was evaluated with the adsorption isotherms. In this case, the Freundlich isotherm was used. The Table 4 compares the trend of each carbon. From Figure 4, it is possible to notice that the most efficient carbon is the ST100 which shows a removal ability of about 14 mg sCOD/g. Even if the ST100 is a carbon with the lower BET area, the results show a better removal efficiency in terms of sCOD. Furthermore, it is evident that with higher doses of carbon, the removal efficiency is almost stable.

Carbon	**Model**	**Equation**	**R^2**
ST300 8x30	Freundlich	0.0189x+0.3217	0.0012
ST300 12x40	Freundlich	1.3019x-0.7448	0.6329
STW400 8X30	Freundlich	1.044x-0.6649	0.89
STW400 12x40	Freundlich	0.3907x-0.1849	0.3007
ST100 8x30	Freundlich	1.7361x-1.6533	0.8348

Table 4 Freundlich isoterms trend for each GAC

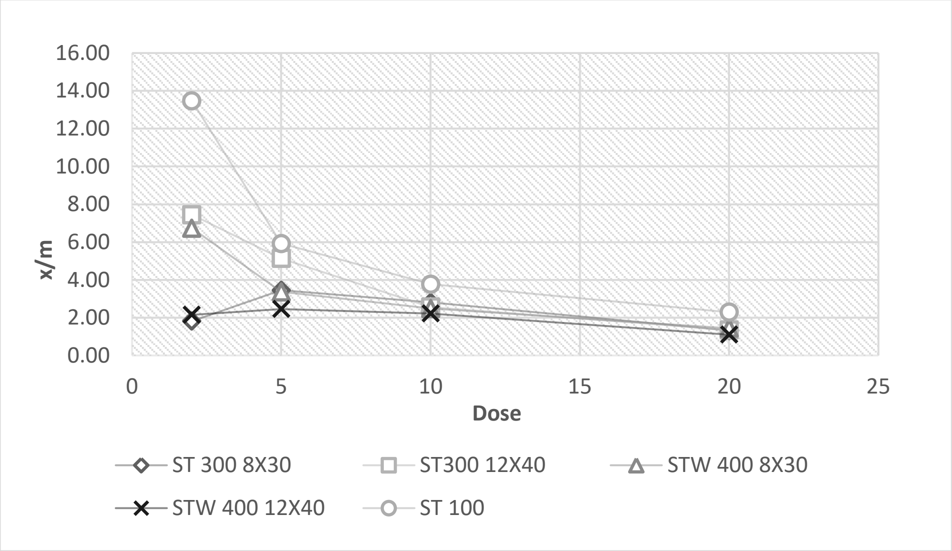

Figure 4 Comparison of adsorption capacity (sCOD) for each GAC

Regarding the adsorption of metals, it was noticed that most perfomant was ST300 8x30 with removal efficiency of about 80% for Mn and Cd and with efficiency of about 40% for Cr. For the carbon ST100 8x30 (which showed the best performance in terms of sCOD removal) it was noticed no removal effect for Cd, meanwhile it was noticed a maximum removal efficiency of 50% for Mn and 30% for Cr.

HC batch experiments

Consistently with results of previous studies [14,15], the pH of all the HC is relatively acid increasing during the test time, as shown in Table 5.

Type	pH start	pH 1 h	pH 2 h	pH 3 h
HC 190°	5.08	5.72	5.81	5.94
HC 250°	5.28	6.04	6.19	6.35

Table 5 pH trend for HC in distilled water

The first batch test (Test 0_A_HC) was carried out in order to wash the non-activated HC in distilled water. The pH was measured at the beginning of the test and at the end. The initial pH was around 6.5 and the final was 8.8. As it is possible to see from the Figure 5, the concentration of sCOD release in liquid phase reached about 700 mg/L with the HC190° at the concentration of 5 g/L. Also, as could be expected, the maximum release is reached at higher HC concentrations both for HC250° and HC190°. The equilibrium condition is reached around 10 and 30 minutes of contact time. At same concentrations, the HC250° showed less sCOD release compare to HC190°, probably caused from the lower residual organic content at higher HC process temperature. At the end of the test, the used HC was recovered and then dried at 105 °C for the subsequent test.

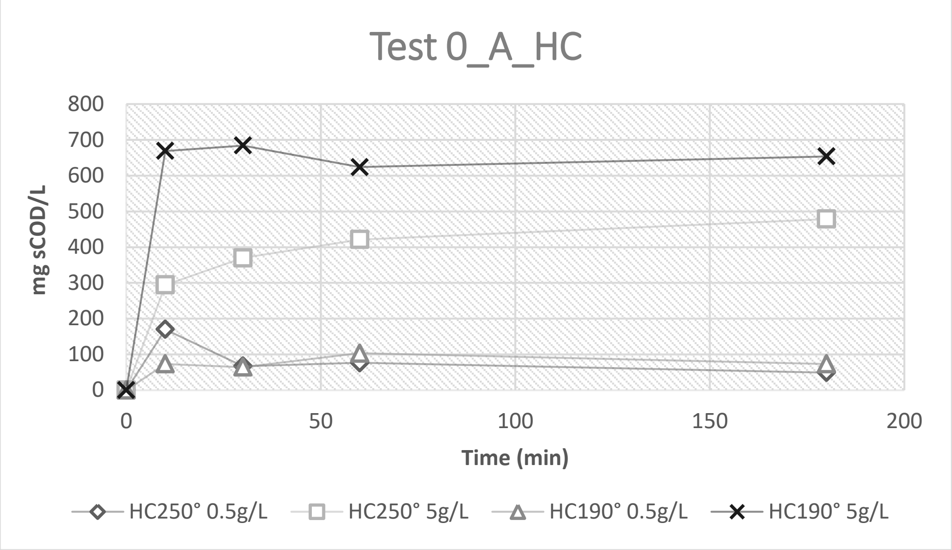

Figure 5 Test 0_A_HC, behaviour of sCOD during three hours batch test

The second test (Test 0_B_HC) was done in order to evaluate the sCOD trend using the washed HC produced after the previous Test 0_A_HC. The sCOD values, at the same previous HC concentrations, show a net decrement of release phenomena. For both HC the maximum sCOD reached at the concentration of 5 g/L is around 150 mgCOD/L. As it is possible to see from the Figure 6, after 10 minutes of contact time the system reached the equilibrium. Also, with low dosage of HC (0.5 g /L) the release of sCOD was not detected. The tests show that the optimal ratio adosrbent/water is about 0.5 g of adsorbent for each L of water used.

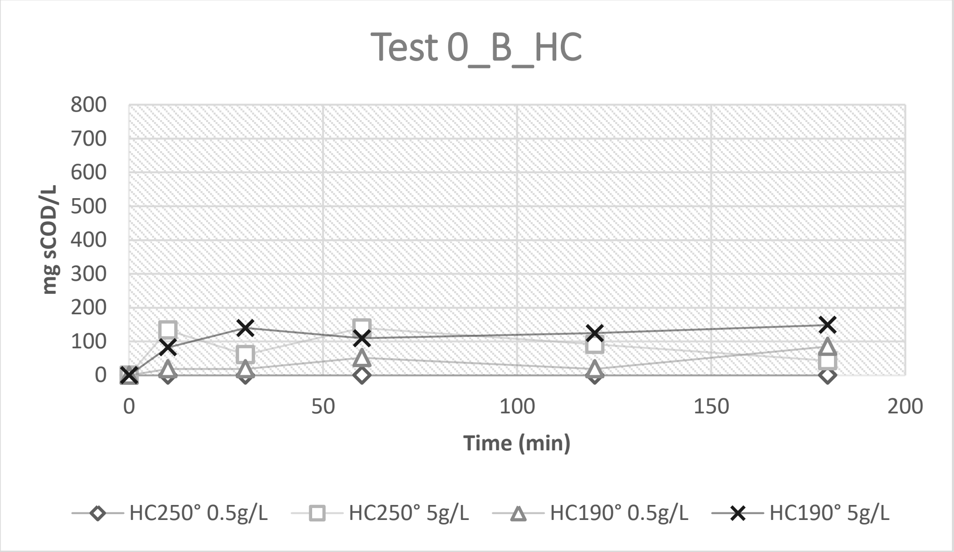

Figure 6 Test 0_B_HC, behaviour of sCOD during three hours batch test

In order to understand the behavior of HC with wastewater, real influent was used (Test 1_HC, 0.8 L of volume) at the same concentrations of HC (0.5 and 5 g/L) recovered from Test 0_A_HC (washed HC). The initial pH was 7.3 and at the end of the test was 8. As is shown by Figure 7, after 10 minutes of contact time, the removal is minimum for both HC at the concentration of 5 g/L. It is consistent with previous test carried out in distilled water. On the contrary, at lower concentrations of both HC, the removal efficiency reached about 65%. This is due the fact that this concentration of HC had the optimal ratio adsorbent/water. It is evident that after about 10-20 minutes of contact time, the removal efficiency does not change.

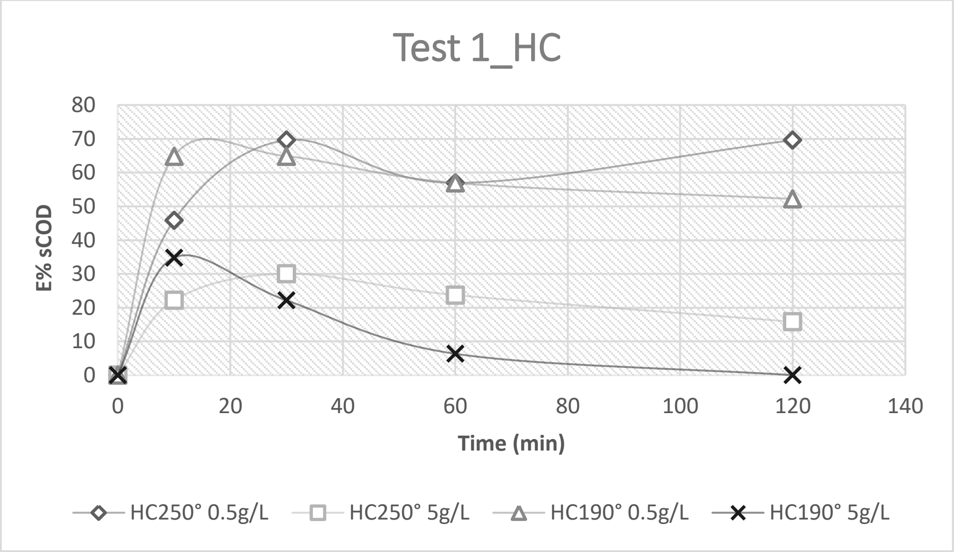

Figure 7 Test 1_HC, behaviour of sCOD during two hours batch test

In order to verify the HC behavior at different COD concentrations, HC was used also with diluted wastewater (from Villa Bagatta CSO plant, Lazise, Italy, Test 2_HC). The results (no showed) displayed no adsorption of soluble COD. It is possible to assert that the not-activated HC has ability to adsorb only after correct ratio of adsorbent/water washing step. In addition, this adsorption is evident only with influent characterized by high COD concentrations.

In order to verify the heavy metals removal, it was performed a batch test adding known concentrations of metals (Test 3_HC, Fig. 8). The adsorption of metal with new adsorbents represents a low cost and easy operating method, if compared with other technology [16]. For this test was used the concentration of HC that had the best behavior in terms of sCOD removal (0.5 g/L). For this study, Mn was used as a representative micropollution present in previous CSO analysis and as reported in literature [17, 18]. For each batch adsorption test, the pH was adjusted to a value of 7-7.5 adding NaOH (30%).

Fig. 8 shows the behavior of Mn adsorption with 0.5 g/L of HC. As reported in the previous characterization data, both HC has not Mn in their elemental composition. The test was performed with two concentrations of metal (around 2 and 15 mg/l). As for sCOD, the adsorption effect is more evident when the concentrations are lower than 15 mg/L of metal. No adsorption phenomena were detected for Zn.

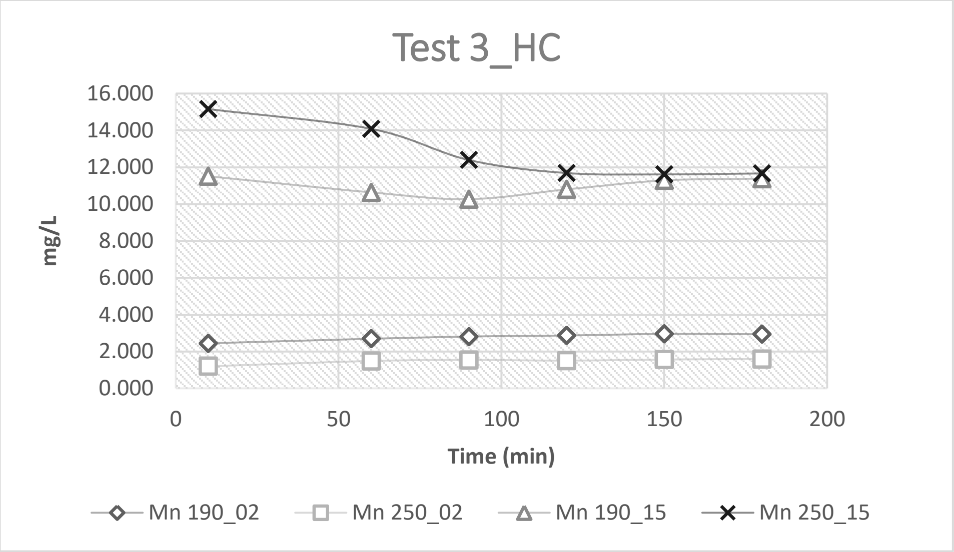

Figure 8 Test 3_HC, behaviour of Mn during three hours batch test

CONCLUSION

Interesting results for non-activated HC as adsorption media for sCOD were found but only for higher initial concentrations. The best results were obtained with lower HC concentrations (0.5 g/L) with the optimal washing ratio of 0.5 g of adsorbent for each L of washing water. Sligly removal of Manganese was detected. Further experiments will be carried out to better identify the non-activated HC potentiality, also at higher concentrations with correct washing ratio. Regarding the commercial GAC, the best adsorption efficiency was evaluated for the carbons ST100 8x30 and ST300 8x30. These second tests were used to design the activated carbon unit in the demonstrative site of Villa Bagatta for the CSO treatment.

ACKNOWLEDGMENTS

This study was carried out within the framework of the “INTCATCH” Innovation Action, which has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 689341. The reviewers are kindly acknowledged for the valuable and highly constructive comments.

REFERENCES

1. www.eureau.com
2. Chhetri, R. K., Thornberg, D., Berner, J., Gramstad, R., Öjstedt, U., Sharma, A. K., & Andersen, H. R. (2014). Chemical disinfection of combined sewer overflow waters using performic acid or peracetic acids. Science of the Total Environment, 490, 1065-1072.

3. Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. Journal of environmental management, 92(3), 407-418.
4. Masi, F., & Martinuzzi, N. (2007). Constructed wetlands for the Mediterranean countries: hybrid systems for water reuse and sustainable sanitation. Desalination, 215(1-3), 44-55.
5. Koottatep, T., Fakkaew, K., Tajai, N., & Polprasert, C. (2017). Isotherm models and kinetics of copper adsorption by using hydrochar produced from hydrothermal carbonization of faecal sludge. Journal of Water Sanitation and Hygiene for Development, 7(1), 102-110.
6. Kambo, H. S., & Dutta, A. (2015). A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. Renewable and Sustainable Energy Reviews, 45, 359-378.
7. Purnomo, C. W., Castello, D., Fiori, L. (2018). Granular activated carbon from grape seeds hydrothermal char. Applied Sciences, 8, 331.
8. Fiori, L., Basso, D., Castello, D., Baratieri, M. (2014). Hydrothermal carbonization of biomass: design of a batch reactor and preliminary experimental results. Chemical Engineering Transactions, 37, 55-60.
9. Basso, D., Weiss-Hortala, E., Patuzzi, F., Castello, D., Baratieri, M., Fiori, L. (2015). Hydrothermal carbonization of off-specification compost: a byproduct of the organic municipal solid waste treatment. Bioresource Technology, 182, 217-224.
10. Spataru, A., Jain, R., Chung, J. W., Gerner, G., Krebs, R., & Lens, P. N. (2016). Enhanced adsorption of orthophosphate and copper onto hydrochar derived from sewage sludge by KOH activation. RSC Advances, 6(104), 101827-101834.
11. American Public Health Association, American Water Works Association, Water Pollution Control Federation, & Water Environment Federation. (1915). Standard methods for the examination of water and wastewater (Vol. 2). American Public Health Association.
12. Volpe, M., Fiori, L. (2017). From olive waste to solid biofuel through hydrothermal carbonisation: the role of temperature and solid load on secondary char formation and hydrochar energy properties. Journal of Analytical and Applied Pyrolysis, 124, 63-72.
13. Volpe, M., Goldfarb, J.L., Fiori, L. (2018).Hydrothermal carbonization of Opuntia ficus-indica cladodes: Role of process parameters on hydrochar properties. Bioresource Technology, 247, 310-318.
14. Fang, J., Gao, B., Chen, J., & Zimmerman, A. R. (2015). Hydrochars derived from plant biomass under various conditions: Characterization and potential applications and impacts. Chemical Engineering Journal, 267, 253-259.

15. Reza, M. T., Rottler, E., Herklotz, L., & Wirth, B. (2015). Hydrothermal carbonization (HTC) of wheat straw: Influence of feedwater pH prepared by acetic acid and potassium hydroxide. Bioresource technology, 182, 336-344.
16. Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: a review. Journal of hazardous materials, 97(1-3), 219-243.
17. Gasperi, J., Garnaud, S., Rocher, V., & Moilleron, R. (2008). Priority pollutants in wastewater and combined sewer overflow. Science of the total environment, 407(1), 263-272.
18. Schertzinger, G., Ruchter, N., & Sures, B. (2018). Metal accumulation in sediments and amphipods downstream of combined sewer overflows. Science of The Total Environment, 616, 1199-1207.