Herbicide Removal from Water: Investigating the Potential of Electrochemistry and Hydrochar-based Activated Carbon

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Terbuthylazine has been introduced to replace atrazine in most of the EU countries; nowadays, this herbicide is one of the most frequently detected in environmental waters. The persistence and the endocrine disruptor activity of this chemical of emerging concern have been established. Conventional treatments applied in drinking water plants do not lead to the complete removal of pesticides and among them, adsorption provides the greatest efficiency. Hydrochar obtained through the hydrothermal carbonization of sewage sludge has been activated and its adsorption capacity has been tested. Moreover, an innovative electrochemical reactor with a Solid Polymer Electrolyte (SPE) has been applied for removing terbuthylazine from an aqueous medium. The activated hydrochar demonstrated an adsorption capacity of 422 mg g^{-1}, reached in 6 hours. Considering the reduction of the volume of sludge to be disposed of obtained if hydrothermal carbonization is carried out, and the thermovalorization of the exhausted hydrochar if used for pollutant removal, further analysis is encouraged to evaluate its effectiveness as adsorbent media in filtration vessels. Up to 88% of the herbicide has been completely removed by the electrolytic treatment in the first hour of treatment, while only 1% has been converted in minor metabolites. Both the sorbent and the advanced oxidation technique investigated here could be applied for the removal of other pesticides and drugs metabolites in water treatment facilities, while the fast removal attained by the SPE technology also offers a prospective for the in-situ remediation of pesticides-polluted groundwater.

1. Introduction

The triazinic ring, preserved in the terbuthylazine (TBA) structure, as well as in many of its metabolites, has been associated with toxicity and oestrogenicity (Pereira et al., 2015). Indeed, TBA is a chemical of emerging concern because of its persistence, toxicity to living organisms at low doses (Choi et al., 2012; Eullaffroy and Vernet, 2003) and high long-term risks to aquatic organisms (Kock-Schulmeyer et al., 2014), mammals, non-target plants and non-target soil macroinvertebrates (Bottoni et al., 2013). The potential risk of bioaccumulation is confirmed by the high octanol–water partition coefficient (Baillie, 2016). Notwithstanding food pollution is a well-recognized issue (Ling, 2018), there is still no information related to the impact on human health due to the intake of metabolites absorbed by the crops, posing a relevant gap in the impact assessment methods of agricultural systems (Tasca et al., 2017).

Chlorination is widely used in drinking water plants, but only 30% of TBA was removed from natural water when NaClO was tested as an oxidizing agent. Adsorption on active carbon is influenced by solution pH (Hnatukova et al., 2011); powered active carbon was tested on polluted natural waters, attaining 60% of herbicide adsorption (Ormad et al., 2008). Several weeks are required to obtain more than 70% degradation in biofilters (Suciu et al., 2013). Hydrogen peroxide alone has no appreciable effect, as demonstrated on the oxidation groundwater samples (TBA concentration: 10 µg L^{-1}) by Sorlini and co-workers (Sorlini et al., 2014). Direct photolysis of 5 mg L^{-1} of TBA in a 250 mL reactor did produce significant degradation only applying an UV dose of 2002 mJ cm^{-2}, significantly higher than those commonly applied in drinking water disinfection, or by the addition of H$_2$O$_2$ (Alvarez et al., 2016; Quinones et al., 2015; Sorlini et al., 2014). Up to 92% of TBA

was removed within 90 mins by photocatalytic degradation over TiO_2 (1.0 g L^{-1}) and with the addition of H_2O_2 and $NaBrO_3$ to reduce the recombination of H^+ and e^-. Most of the removal efficiency has been attributed to the interaction with hydroxyl radicals; the cleavage of the side chain is followed by the substitution of Cl atom by hydroxyl radicals, hydroxylation and abstraction of H atoms (Yang et al., 2016). Photodegradation of TBA was successfully conducted also by the use of a TiO_2/chitosan thin layer; however, cyanuric acid was obtained as final product and this compound cannot be removed by either photolysis or photocatalytic degradation (Le Cunff et al., 2015). A TBA removal efficiency of 45% was reached by ozonation of natural water (Ormad et al., 2008), while a complete destruction of the herbicide was attained within 2 h by single ozonation, O_3/H_2O_2 process and heterogeneous catalytic ozonation with AC, Multi Walled Carbon Nanotubes and TiO_2 as catalysts (Alvarez et al., 2016). Solar-driven techniques based on ozonation coupled with TiO_2 photocatalysis have also been successfully tested, obtaining a complete removal of TBA within 90 mins (Quinones et al., 2015). However, by products have been barely investigated, notwithstanding the fact that some of them have demonstrated an oestrogenic activity comparable to atrazine (Pereira et al., 2015). Very recently, promising results have been obtained by electrolytic radicals production by Clematis and co-workers (Clematis et al., 2017) and Klidi et al. (Klidi et al., 2019); however, this technology has not been investigated on the removal of TBA.

Considering the proven efficiency of adsorption on activated charcoal and the promising results obtained by advanced oxidation techniques, these two options deserve particular attention. With regard to the former technique, hydrothermal carbonization (HTC) is gaining growing attention, and an activation process of the carbonaceous material obtained through this process could lead to the production of valuable adsorbents. HTC is a thermo-chemical conversion for recovery and enhancement of biomass, included sewage sludge. The process occurs under autogenous pressure at temperatures ranging from 180 to 250 °C in a biomass-water mixture, resulting mainly in the formation of solid particles (hydrochar) and a liquid fraction (bio-oil mixed with water). Highly porous activated carbons can be produced by the activation of hydrochars; Puccini and co-workers recently developed an activated carbon using hydrochar from green waste as precursor, with a BET surface area of 1739 $m^2 g^{-1}$, which demonstrated up to 97.9 % removal efficiency when tested on an aqueous solution of atrazine (Puccini et al., 2018). Regarding advanced oxidation techniques, oxidants needs to be produced in-situ in water treatments plants, due to its limited half-life. Electrolytic production of oxidants avoids the transportation of potentially dangerous chemicals, and no outside contamination is introduced in the system, as the source of oxidants is the treated media itself. Moreover, the oxidant is dissolved in water as soon as it is formed, resulting in a minimum amount of equipment required for the process (Stanley, 2004). This paper describes the activation process of a hydrochar obtained from the hydrothermal carbonization of sewage sludge and explores its adsorption performance through the removal of TBA from an aqueous solution. Moreover, an electrochemical reactor equipped with a solid polymer electrolyte (SPE) has been tested with the same scope, focusing also on the by-products generated.

2. Experimental

2.1 Materials

Hydrochar obtained from hydrothermal carbonization of sewage sludge has been used as the precursor for the preparation of active carbon. Potassium hydroxide (KOH - Sigma Aldrich Co. Llc, Analytical grade chemicals) has been used as the activating agent. Terbuthylazine (PESTANAL, Analytical standard) has been supplied by Sigma Aldrich Co. Llc.

2.2 Hydrochar activation and characterization

Hydrochar samples have been dried at 105 °C for 24 h, then crushed and sieved to particle size minor than 75 µm. The so-obtained powder has been mixed with potassium hydroxide at a ratio hydrochar / KOH = 0.5. The mixture has been placed in oven at a 650 °C for 150 min, under nitrogen flow (180 mL min^{-1}) and cooled down at a ramp of 5 °C min^{-1}. The obtained samples have been washed with HCl 5 M and then with distilled water, to remove the acid. Proximate analyses have been conducted according to the recent work of Puccini et al. by using a thermogravimetric analyser (TGA Q500 TA Instruments) (Puccini et al., 2018). Activated samples have been heated from 30 to 900 °C at a ramp of 20 °C min^{-1}, under nitrogen flow (100 vol%), to measure moisture and volatile matter content. Then, the temperature has been decreased to 800 °C and the gaseous flow was switched to air, with the aim to measure fixed carbon and ash content.

2.3 Adsorption tests

An aqueous solution of 4 mg/L of terbuthylazine has been maintained under stirring in an open container, at room temperature, for 24 h, after the addition of 3 mg of the activated hydrochar. Experiments have been carried out at room temperature (approximately 20 °C). Tap water has been used to prepare the solution

analysed, with the aim to obtain results more representative of a plant inlet stream. The procedure has been repeated using a sample of the virgin hydrochar, to estimate the effect of the activation process on the adsorption capacity of the material. Hydrochar samples have been meshed and a granulometry between 63 and 212 µm has been selected for the adsorption tests. A spectrophotometer Shimadzu UV-1700 PharmaSpec has been used to measure the aqueous concentration of the herbicide.

2.4 Electrolytic reactor

The tests have been carried out in an open glass reactor. A 300 mL solution of 4 mg of terbuthylazine has been continuously stirred for 1 hour and electrolysis has been operated at galvanostatic condition. The herbicide has been dissolved in tap water for the same reason explained in Section 2.2. A constant current of 100 mA was applied. A Nafion® N324 ion exchange membrane, sandwiched between a Nb/Boron-Doped Diamond mesh anode and a Ti/RuO2 mesh electrode (Figure 1), was immersed in the aqueous media. Details of the apparatus are described in the recent works of Clematis (Clematis et al., 2017) and Klidi (Klidi et al., 2019). The aqueous concentration of the terbuthylazine and treatment intermediates have been measured by using a GC-MS spectrophotometer. The choice of gas chromatography was due to the purpose of investigating the formation and the evolution of minor metabolites along the treatment, which was expected to be below the limit of detection of a UV-Vis spectrophotometer.
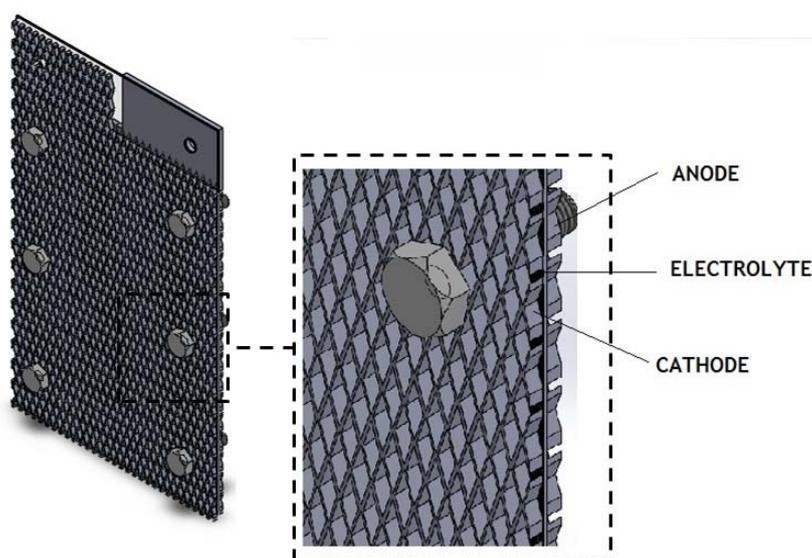

Figure 1: Detail of the electrolytic reactor (Clematis et al., 2017)

3. Results

3.1 Hydrochar activation and adsorption tests

The yield of the activation step of hydrochar obtained from sewage sludge was 21.17 %. The results of the thermogravimetric analysis are presented in Table 1: the activation phase considerably reduces the percentage content of moisture, volatile matter and ash. Values are expressed as weight percentage dry based.

The enhanced porosity of the activated material is ascribed to the reaction of KOH with C under inert conditions, which causes the development of different potassium species (K_2O, K, K_2CO_3) during the activation step. The diffusion of these species into the hydrochar framework likely widens the existing pores, leading to a well-developed micropore structure, as recently confirmed by Scanning Electron Microscope images of activated hydrochars obtained from green waste (Puccini et al., 2018). Hence, enhanced adsorption capacity is expected by the activated material, if compared with the virgin hydrochar.

Figure 2 shows the results of the adsorption batch tests. The virgin hydrochar adsorbed 219 mg g^{-1}, reaching 70 % of its adsorption capacity in the first 30 min. The activated material exhibited a specific uptake of 422 mg g^{-1}, with most of the removal attained in the first 95 min. The maximum removal was reached within the first 6 h, for both the samples tested.

Table 1: Proximate analysis of the hydrochar and activated hydrochar sample

Proximate analysis parameters	Hydrochar (wt%)[*]	Activated Hydrochar (wt%)*
Moisture	1.69	5.36
Volatile matter	55.91	21.94
Ash	38.31	26.03
Fixed carbon	4.09	46.67

[*] dry basis

3.2 Electrolytic radicals production

Notwithstanding the very low value of the electric current applied, 61 % of terbuthylazine has been removed by electrolytic radicals production in the first 30 mins of treatment. The main removal mechanism is ascribed to the action of the hydroxyl radicals produced at the anode surface. The rate of removal decreased in the following mins, and 89 % of the herbicide disappeared at the end of the treatment, as it can be seen in Figure 3. However, as discussed in Section 1, the disappearance of the target substance can be due only to its conversion in a chemical with similar toxicity or accompanied by the generation of significative amounts of by-products with proven or unknown associated risk for humans and wildlife. Hence, the efficiency of the proposed treatment cannot be discussed only by its removal rate. Treatment metabolites and respective concentrations have been identified and reported in Table 2.

Table 2: Terbuthylazine and treatment intermediates. detected by GC-MS.

Time (min)	0	30	45	60
Terbuthylazine (μg L^{-1})	3780	1474	722	426
2-chloro-4-amino-6-terbuthylamino-1,3,5-triazine (μg L^{-1})	2	42	41	35
2-chloro-4,6-amino-1,3,5-triazine (μg L^{-1})	0	0	0	2
2-chloro-4-ethylamino-6-amino-1,3,5-triazine (μg L^{-1})	0	1	1	1
2-chloro-4-acetamido-6-terbuthylamino-1,3,5-triazine (μg L^{-1})	0	5	5	5

The oestrogenic activity of these substances has been recently confirmed by Pereira and co-workers by yeast oestrogen screen tests (Pereira et al., 2015). The main by-product found was 2-chloro-4-amino-6-terbuthylamino-1,3,5-triazine, also known as desethylterbuthylazine, which is one of the most detected compound in many European surface waters and groundwaters (Tasca et al., 2018). The proposed technique is highly effective, as the disappearance of terbuthylazine is accompanied only by the generation of a very small amount of treatment intermediates, less than 1% of the initial herbicide concentration. Electrolytic radicals productions partially degraded the desethylterbuthylazine formed in the first 30 mins, while it had no discernable effect on the other metabolites detected.
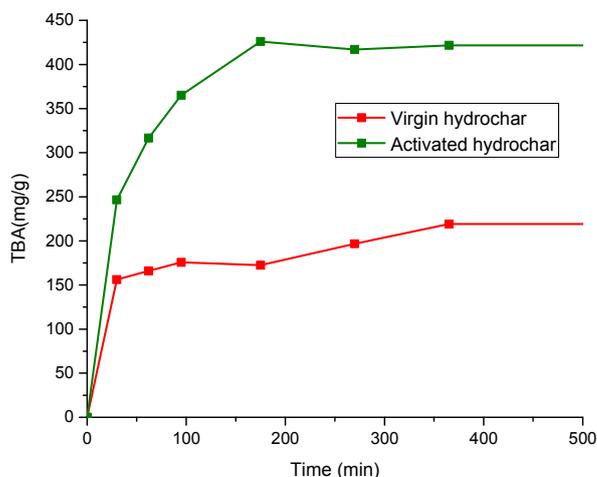

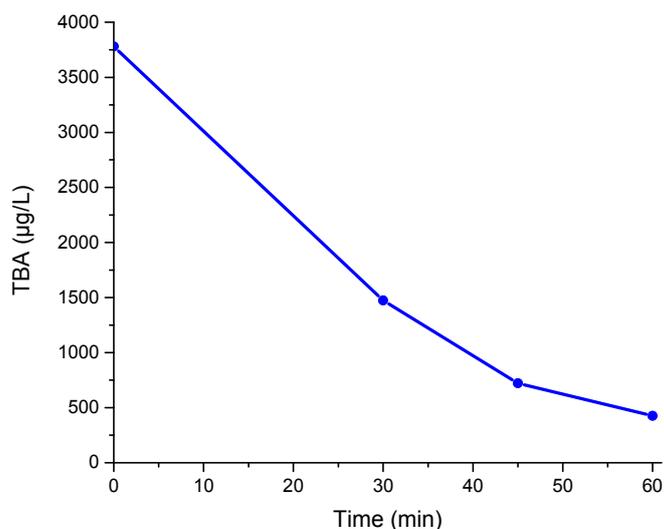*Figure 2: Terbuthylazine adsorption on virgin and activated hydrochar*

Figure 3: Terbuthylazine detected at different treatment times. Applied current: 100 mA

4. Conclusions

Hydrochar obtained by the hydrothermal carbonization of sewage sludge has been activated and tested for the adsorption of the herbicide terbuthylazine. The removal of the herbicide was carried out also by the use of an innovative electrochemical cell. equipped with a solid polymer electrolyte.

The developed sorbent revealed a good adsorption capacity, as 86 % of terbuthylazine have been removed from the polluted media within less than 2 hours. Regeneration options may be explored and compared with new hydrochar production and activation, coupled with the thermovalorization of the exhausted sorbent. The electrolytic cell provided an 89 % abatement in 1 hour of treatment, with low energy requirements, no need of additional chemicals and no waste generation. Moreover, the removal of terbuthylazine is not due to its conversion in a chemical with similar toxicity and it is not accompanied by the generation of a significative amount of toxic by-products. Even considering the same target, i.e.: pesticide removal from water, technical and economic issues need to be evaluated by a case-specific approach. The use of hydrochar-based active carbon offers good adsorption capacity and well fits the circular economy approach, while electrolytic radicals production provides a fast abatement with no need for additional operations as filter backwashing and sorbent regeneration. The latter technique would likely be more efficient on highly contaminated streams, due to its electricity requirements.

References

Alvarez, P.M., Quinones, D.H., Terrones, I., Rey, A., Beltran, F.J., 2016, Insights into the removal of terbuthylazine from aqueous solution by several treatment methods, Water Research, 98, 334–343. doi.org/10.1016/j.watres.2016.04.026

Baillie, B.R., 2016, Herbicide concentrations in waterways following aerial application in a steepland planted forest in New Zealand, New Zealand Journal of Forestry Science, 46. doi.org/10.1186/s40490-016-0072-0

Bottoni, P., Grenni, P., Lucentini, L., Caracciolo, A.B., 2013, Terbuthylazine and other triazines in Italian water resources, Microchemical Journal, 107, 136–142. doi.org/10.1016/j.microc.2012.06.011

Choi, C.J., Berges, J.A., Young, E.B., 2012, Rapid effects of diverse toxic water pollutants on chlorophyll a fluorescence: Variable responses among freshwater microalgae, Water Research, 46, 2615–2626. doi.org/10.1016/J.WATRES.2012.02.027

Clematis, D., Cerisola, G., Panizza, M., 2017, Electrochemical oxidation of a synthetic dye using a BDD anode with a solid polymer electrolyte, Electrochemistry Communications, 75, 21–24. doi.org/10.1016/j.elecom.2016.12.008

Eullaffroy, P., Vernet, G., 2003, The F684/F735 chlorophyll fluorescence ratio: a potential tool for rapid detection and determination of herbicide phytotoxicity in algae, Water Research, 37, 1983–1990. doi.org/10.1016/S0043-1354(02)00621-8

Hnatukova, P., Kopecka, I., Pivokonsky, M., 2011, Adsorption of cellular peptides of Microcystis aeruginosa and two herbicides onto activated carbon: Effect of surface charge and interactions, Water Research, 45, 3359–3368. doi.org/10.1016/j.watres.2011.03.051

Klidi, N., Clematis, D., Carpanese, M.P., Gadri, A., Ammar, S., Panizza, M., 2019, Electrochemical oxidation of crystal violet using a BDD anode with a solid polymer electrolyte, Separation and Purification Technology, 208, 178–183. doi.org/10.1016/j.seppur.2018.03.042

Kock-Schulmeyer, M., Ginebreda, A., Postigo, C., Garrido, T., Fraile, J., de Alda, M.L., Barcelo, D., 2014, Four-year advanced monitoring program of polar pesticides in groundwater of Catalonia (NE-Spain), Science of The Total Environment, 470, 1087–1098. doi.org/10.1016/j.scitotenv.2013.10.079

Le Cunff, J., Tomasic, V., Wittine, O., 2015, Photocatalytic degradation of the herbicide terbuthylazine: Preparation, characterization and photoactivity of the immobilized thin layer of TiO2/chitosan, Journal of Photochemistry and Photobiology a-Chemistry, 309, 22–29. doi.org/10.1016/j.jphotochem.2015.04.021

Ling, W., 2018, Risk Assessment of Chemical Pollution in Organic Food, Chemical Engineering Transactions, 67, 145–150.

Ormad, M.P., Miguel, N., Claver, A., Matesanz, J.M., Ovelleiro, J.L., 2008, Pesticides removal in the process of drinking water production, Chemosphere, 71, 97–106. doi.org/10.1016/j.chemosphere.2007.10.006

Pereira, S., Reis, T., Souza, B., Dantas, R., Azevedo, D., Dezotti, M., Sans, C., Esplugas, S., 2015, Oestrogenicity assessment of s-triazines by-products during ozonation, Environmental Technology, 36, 1538–1546. doi.org/10.1080/09593330.2014.995235

Puccini, M., Stefanelli, E., Tasca, A.L., Vitolo, S., 2018, Pollutant Removal from Gaseous and Aqueous Phases using Hydrochar-based Activated Carbon, Chemical Engineering Transactions, 67, 637–642.

Quinones, D.H., Rey, A., Alvarez, P.M., Beltran, F.J., Puma, G.L., 2015, Boron doped TiO2 catalysts for photocatalytic ozonation of aqueous mixtures of common pesticides: Diuron, o-phenylphenol, MCPA and terbuthylazine, Applied Catalysis B-Environmental, 178, 74–81. doi.org/10.1016/j.apcatb.2014.10.036

Sorlini, S., Gialdini, F., Stefan, M., 2014, UV/H2O2 oxidation of arsenic and terbuthylazine in drinking water, Environmental Monitoring and Assessment, 186, 1311–1316. doi.org/10.1007/s10661-013-3481-z

Suciu, N.A., Ferrari, F., Vasileiadis, S., Merli, A., Capri, E., Trevisan, M., 2013, Pesticides water decontamination in oxygen-limited conditions, Journal of Environmental Science and Health Part B, 48, 793–799. doi.org/10.1080/03601234.2013.781346

Tasca, A.L., Nessi, S., Rigamonti, L., 2017, Environmental sustainability of agri-food supply chains: An LCA comparison between two alternative forms of production and distribution of endive in northern Italy, Journal of Cleaner Production, 140, 725–741. doi.org/10.1016/j.jclepro.2016.06.170

Tasca, A.L., Puccini, M., Fletcher, A., 2018, Terbuthylazine and desethylterbuthylazine: Recent occurrence, mobility and removal techniques, Chemosphere, 202, 94–104. doi.org/10.1016/j.chemosphere.2018.03.091

Yang, H., Wei, H.Q., Hu, L.T., Liu, H.J., Yang, L.P., Au, C.T., Yi, B., 2016, Mechanism for the photocatalytic transformation of s-triazine herbicides by center dot OH radicals over TiO2, Chemical Engineering Journal, 300, 209–216. doi.org/10.1016/j.cej.2016.04.099