The Catcher in the Water: Magnetic Biochar for the Treatment of Wastewater

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Abstract

Magnetic biochar (MBC) is obtained from the same raw materials used to have biochar. With inclusion of iron or addition of magnetic precursors, biochar turns into a material which has magnetic separation capabilities. Defined as a win-win material for the treatment of wastewater pollution, here we consider MBC for those specific applications where it is acting as a "catcher in the water".

Keywords: Wastewater, Biochar, Magnetic Biochar.

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1. Introduction

Magnetic biochar (MBC) is a material possessing magnetic separation capabilities, that can be obtained from the same raw materials used to have biochar. Several techniques exist to produce it. As explained by Xiao et al., 2023, the preparation of MBC requires the inclusion of iron in the raw material or the addition of magnetic precursors (Niu et al., 2020). Two types of feedstocks are involved in the preparation: the iron-containing waste biomass and the non-iron-containing biomass. In the second case, the raw material requires a magnetic precursor for creating magnetic features. The preparation methods in both cases have been clearly illustrated by Xiao et al., 2023. Of MBC, we discussed (Sparavigna, 2023) about its use in composites for shielding electromagnetic interferences and absorption of microwaves. Here we consider this magnetic material in its role of “catcher in the water”, that is in the treatment of wastewater pollutants. Actually, the use of waste biomass to produce biochar useful to treat wastewater can be considered as a win-win approach (Xiao et al., 2023) to the persistent problems regarding water pollution.

2. Biochar

Biochar is a solid material which is consisting of the fine-grained residues of biomass pyrolysis. It is the product of the thermochemical decomposition of biomass at moderate temperatures (350–700°C) under oxygen-limiting conditions (Brassard et al., 2019). Besides biochar, liquid (bio-oil) and gas (syngas) products are obtained from the thermal decomposition (Han & Kim, 2008, Ok et al., 2018, Bartoli et al., 2020). Today, the main use of biochar is as amendment in agricultural soils, because of its high carbon content, stability, porosity and surface area (Brassard et al., 2019, Ok et al., 2015). Because of its relevantly functionalized surface, biochar is exhibiting compatibility with cement, asphalt, and polymer (Tan et al., 2021, Zhao et al., 2014, Zhang et al., 2018, Das et al., 2021). In Zhang et al., 2022, we can find a study regarding the state-of-the-art biochar-enhanced construction materials (see also Danish et al., 2021, Maljaee et al., 2021, Tan et al., 2021). For other non-soil applications of biochar, such as energy storage, polymeric composites, recycling materials, sensors and catalyst production, reviews have been given by Ziegler et al., 2017, and Lepak-Kuc et al., 2021.

The biochar carbon-based material is remarkable for its hierarchical porous structure, possessing a large specific surface area based on the presence of a mesoporous framework. For this reason, biochar can be used for producing shape-stabilized phase change materials, SSPCMs (Sparavigna, 2022). The biochar mesopores can encapsulate the liquid phase of PCMs, which are substances absorbing and releasing thermal energy at phase transitions, overcoming the leakage problem of them (Liang et al., 2022, Yang et al., 2019). In the porous framework of biochar, magnetic nanoparticles can be easily incorporated, producing a magnetic biochar which has electromagnetic interference (EMI) shielding features. As previously told, of EMI shielding effectiveness of MBC we discussed recently (Sparavigna, 2023). In this research, we have encountered encapsulated Fe_3O_4 nanoparticles added to increase biochar electric permittivity and magnetic permeability.

3. Applications of magnetic biochar

The article by Thines et al., 2017, is a rich review about the synthesis of magnetic biochar. We can find a detailed discussion of the production methods with related references. The applications of MBC mentioned by Thines and coworkers are for the treatment of wastewater and for the use in polymer composites to obtain super-capacitors. MBC is told being used as an adsorbent for water treatment in the cases of its contamination. Pollution can come from “the discharge of hazardous effluent such as heavy metals from industries such as mining, battery, metal plating and paper industries or organic substances and dyes from textile industries into the nearby source of water without any treatment" (Thines et al. are mentioning Inyang et al., 2012). Various wastewater treatment techniques (ion exchange, membrane filtration, biological treatment, adsorption) are mentioned and references provided, but "Every method of wastewater treatment was found to have its own set of advantages and disadvantages" (Thines et al., 2017).

The adsorption process considers solid substances able of attracting molecules to their surfaces. These solids are called "adsorbents", and the adsorbed molecules constitute the "adsorbate". According to Thines and coworkers, the adsorption process obtained by means of solid adsorbents is among the most efficient methods for the wastewater treatment. "The abundantly available biomass", and among them the researchers are mentioning cottonwood, pinewood, corn straw and others (Thines et al., 2017, and references therein), can be used to produce adsorbents. These adsorbents can be turned into magnetic biochar for the removal of arsenic and other metals, that is zinc, lead, cadmium, tin, chromium and copper, “in a simple adsorption process" (Thines et al., 2017). In the case of the textile industry, the water needs to be decontaminated from synthetic dye and finishing compounds, and biochar can be used too.

4. Heavy metals

As told by Yap et al., 2017, adsorption is a trustable technology that industry is preferring because of its low cost and efficiency. Used materials are including activated carbon, fly ash, sewage sludge ash, woody biomass and others, which have a high capability in lead and cadmium removal from wastewater (Yap et al., 2017). Activated carbon has a higher adsorption uptake but it is difficult to be separated from wastewater and therefore it ends being "released with the process sludge into environment, *resulting to secondary pollution*" (Yap et al., 2017). The *magnetic separating technique* is circumventing this pollution, by introducing a magnetic medium (ferric chloride, $FeCl_3$ for instance), to the considered adsorbent in order to separate it from water. To produce "powdered activated carbon, agricultural waste products such as rice husk, maize husk, and coconut-based biosorbents" can be used (Yap et al., 2017).

The article by Yap et al., 2017, describes a magnetic biochar synthesized by a microwave technique, based on the coconut shell (CS). "These newly produced magnetic biochars have high surface area", which "leads to high efficiency in the removal of cadmium and lead from wastewater" (Yap et al., 2017). Coconut shell is the biochar raw material and ferric chloride hexahydrate ($FeCl_3$-$6H_2O$) the magnetic precursor.

The impregnation ratio, IR, between the coconut shell and ferric chloride has fundamental effect on the MBC adsorption capacity of heavy metal ions. "Evaluation of its effect ... can be obtained by altering the impregnation ratio from 0.25 to 0.50. Above IR of 0.50, the adsorption capacity and carbon yield start to decrease" (Yap et al., 2017). Consequently, the optimized adsorption capacity is at IR around 0.5. Yap and coworkers explain that in this manner it is promoted the pore development in biochar, and consequently we have a "dramatic growth in the BET surface area and volume of pores". The adsorption capacity is improved, but beyond IR value of 0.5, "the accessible area decreased drastically" (Yap et al., 2017). It is the excess of $FeCl_3$ which is causing “vigorous gasification reaction”, ruining the carbon framework. An excessive presence of $FeCl_3$ produces side reaction coming from the decomposition of molecules, and the catalytic oxidation damages micro- and macroporous biochar structures (Yap et al., 2017).

Tan et al., 2017, and Ruthiraan et al., 2017, have also developed magnetic biochar for removing cadmium from wastewater. Tan et al. used a synthesis from the rice straw with Fe^{2+}/Fe^{3+} and pyrolysis. The biochar was used as adsorbents for Cd(II), with a high efficiency up to 91 %. Tan and coworkers evidenced a rate much greater than that of the original biochar. Chin et al., 2022, proposed a review about MBC crosslinked chitosan for heavy metal removal from wastewater. Ruthiraan et al., 2017, studied also the removal of methylene blue from wastewater.

Since we have previously mentioned the encapsulated Fe_3O_4 particles, let us consider that in the form of $Fe_3O_4@SiO_2$-NH_2 core-shell magnetic particles, attached on carboxylated biochar, they have been proposed for removing Cr(VI) from acidic solutions by Shi et al., 2018. The Cr (VI) adsorption capacity of this magnetic biochar is surpassing that of the original carboxylated biochar. The characterization of the process has shown that encapsulated Fe_3O_4 particles "not only endowed biochar with perfect magnetic property … but also provided complexing sites for binding Cr(III) cations reduced from Cr(VI) anions” (Shi et al., 2018). Shi and coworkers are describing the Cr(VI) removal in three steps of adsorption of Cr(VI) anions, reduction of these anions to Cr(III) cations and chelation of them by amine groups.

5. Mechanisms

Khan et al., 2020, studied the mechanisms for cadmium adsorption by magnetic biochar composites. The biochar "can immobilize or remove heavy metals” from water. The pristine BC, however, has "limited capability" in removing pollutants, and therefore "needs to be further improved with well-surface properties and novel structures", are telling Khan and coworkers mentioning Song et al., 2014. Literature reports that the surface features of biochar can be improved for what is regarding the adsorption potentiality, "by increasing the number of functional groups and selectivity to remove several pollutants from polluted systems" (Khan et al., 2020, mentioning Ma et al., 2014). Khan and coworkers are providing a list of features which are helpful in removing heavy metals. Among them we find the decoration with iron oxide nanomaterials (Wu et al., 2018, Karunanayake et al., 2018), and the steam-activated BC to remove copper from solutions (Ippolito et al., 2012). "BC modification via activation can increase the surface area, ligand functional group presence, or number of available electrons, all of which help improve heavy metal sorption" (Khan et al. mentioning Ippolito et al., 2012).

Khan and coworkers produced MBC derived from corn straw powder, doped with iron oxide. "The resulting MBC composites manifested *tremendous physicochemical properties* such as more oxygen-containing functional groups, a fine-pore structure, and large surface area". The researchers tell that Cd(II) is successfully adsorbed onto MBC "because of the iron adhering to the BC surface". After cadmium sorption, MBC is collected from the aqueous solution.

Ifthikar et al., 2017, proposed the use of magnetic sewage sludge biochar (MSSBC) to have a fabrication process accompanied by low cost of production, but at the same time a superior adsorption capacity. The heavy metal is Pb(II): "the lead-MSSBC equilibrium was achieved within one hour, owing to the existence of the copious active sites" (Ifthikar et al., 2017). "Mechanism study demonstrated the adsorption involved electrostatic attraction, ion exchange, inner-sphere complexation and formation of co-precipitates at the surface of MSSBC" (Ifthikar et al., 2017). The researchers, Ifthikar et al., are also reporting that "many efforts have been paid to remove heavy metal ions from aqueous solution by magnetic biochars, ... For example, ... [MBC was proposed] ... to eliminate lead and cadmium from wastewater (Yap et al., 2017; Mohan et al., 2014)"; then we have also MBC used for chromium ions (Shang et al., 2016) and arsenic(V) removal (Zhou et al., 2017). However, "Until now, the application of *sewage sludge biochar* modifications remains limited" (Ifthikar et al., 2017).

The article by Yi et al., 2020, is a review about MBC where the adsorption of heavy metals is considered in great detail. Yi and coworkers, after the analysis of available literature, tell that the adsorption capacity of MBC regarding Cr(VI) is comprised between 8.35 mg/g to 220 mg/g, "which further illustrates that the performance of magnetic biochar is greatly affected by different methods of synthesis and raw materials. The mechanism by which Cr(VI) is removed by magnetic biochar involves electrostatic adsorption, reduction, ion exchange, complexation with functional groups and co-precipitation" (Yi et al., 2020). For As(V) and As(III), the adsorption capacity is variable too, depending on the used biochar. "The mechanism of As removal by magnetic biochar mainly includes electrostatic adsorption and complexation with functional groups, and iron oxides play a key role in arsenic removal" (Yi et al., 2020).

The chromium Cr(VI) removal by means of magnetic biochar was proposed by Shang and coworkers, 2016. MBC was obtained from Astragalus membranaceus residue and Fe^{2+}/Fe^{3+} co-precipitation. SEM and spectroscopy analyses proved the adsorbent had iron oxide inside and that a "magnetic" biochar was prepared indeed. X-ray studies "further demonstrated the existence of iron oxide in the magnetic biochar and showed that oxygen-containing groups decreased after adsorption. The maximum Cr(VI) adsorption occurred at pH 2 (23.85 ± 0.23 mg/g)" (Shang et al., 2016). According to Shang and coworkers, "magnetic biochar could be separated easily from water with external magnetic fields and that such a material could be used as a *cost-effective adsorbent* in heavy metal removal applications".

Let us consider again the review by Yi et al., 2020: "The cationic heavy metal pollutants removed by magnetic biochar are mainly Cd(II), Pb(II), Cu(II), Ni(II), Sb(II), Sn(II) and Hg(II), and the efficiency of their removal is influenced by their different physical and chemical properties". About the removal mechanism of these cations by MBC, a list is given: "1) electrostatic adsorption; 2) ion exchange; 3) surface complexation; 4) π-π interaction; 5) internal spherical complexation; 6) hydrogen bonding; and 7) co-deposition" (Yi et al., 2020).

6. Nuclear wastewater

Yi et al., 2020, tell that "magnetic biochar has been used for the removal of the nuclear waste pollutants U(VI) and Eu(III)". Among the mentioned research works we can find those by Hu et al., 2018, Zhu et al., 2018, Li et al., 2019. Liao et al., 2022, are proposing an environmentally friendly magnetic biochar for efficient removal of uranium (VI) from wastewater. The researchers used cow manure to produce biochar, and magnetic iron oxide was added to modify it in the magnetic form. Qasim et al., 2022, produced magnetic biochar obtained from conocarpus erectus leaves to remove cobalt ions. Guo et al., 2023, use lignin-derived magnetic biochar for the separation of Th (IV) and U (VI). Let us add the work by Palansooriya et al., 2022, that discuss the biochar with enhanced functionality for removal of radioactive cesium and strontium from water, and the work by Da et al., 2022, about the prediction of uranium adsorption capacity obtained by means of the machine learning.

Zizhen et al., 2021, about the application of biochar in radioactive wastewater treatment, are giving remarkable conclusions. "The preparation process [of biochar] is environmentally friendly and safe". Biochar possesses excellent adsorption features regarding “metal ions in the process of radioactive wastewater treatment”. Today, the research is mainly focused on “the aspect of modification, discussing the adsorption characteristics and mechanism of biochar, and how to use different modification methods to increase the maximum adsorption capacity of biochar” (Zizhen et al., 2021). However, some key issues exist, and the following aspects need to be considered. According to Zizhen and coworkers, they are:

(1) “it is necessary to … strengthen the selectivity of biochar in radioactive wastewater “, to increase it for “uranium, strontium, cesium, and cobalt ions, and reduce” it for other ions, such as those of sodium, chromium, cadmium, and copper (Zizhen et al., 2021);

(2) With biochar treatments of radioactive wastewater, which are becoming “more and more extensive, the use of amount chemical modification reagents will lead to more by-products”, with a consequent growing of environmental pressure on the use of the treatments. It is therefore fundamental “to avoid or reduce the production of by-products” (Zizhen et al., 2021);

(3) The biochar treatment of radioactive wastewater is a conversion of “large-volume, liquid radioactive waste into small-volume, solid radioactive waste” (Zizhen et al, 2021). Research is required to evaluate the post-treatment of the resulting solid pollutants and by-products;

(4) The time required to have biochar is “relatively long, and the single output is relatively small, which limits the wide application of biochar in radioactive wastewater treatment” (Zizhen et al., 2021). Research is required to reduce cost and time to have a complete radioactive wastewater treatment on large-scale application.

We can add that these issues evidenced by Zizhen et al., 2021, are present also for the use of biochar to remove other pollutants. Costs, quantities and by-products are logistic problems that must be investigated to scale-up from laboratories to civil and industrial installations.

7. Organic pollutants in wastewater

Yi et al., 2020, consider the magnetic biochar as a material possessing good adsorption features with respect to the organic pollutants. MBC is removing antibiotics, organic dyes, pesticides, phenol and organochlorine compounds (Yi et al., 2020, Kumar et al., 2020, Meng et al., 2015). “The mechanism of antibiotic removal” involves “hydrogen bonding, π-π interactions, pore-filling effects, electrostatic adsorption, and hydrophobic interactions” (Yi et al., 2020). MBC are able of adsorbing the organic dyes “rhodamine B, methylene blue, malachite green, acid orange 7 (AO-7), and orange-G”. And other organic pollutants that can be removed by magnetic biochar are “pesticides, phenol, organochlorine, and hormones”, with mechanisms based on “hydrogen bonding, π-π interactions, pore-filling effects, electrostatic adsorption, hydrophobic interactions and reductive dehalogenation” (Yi et al., 2020).

8. Biochar from rice straw

In the previous sections, we have mentioned several mechanisms for adsorption by biochar. A very clear illustration of the related interactions has been given by Foong et al., 2022, in their Figure 4, for metallic and organic pollutants. Foong and coworkers are proposing a review about the production of biochar from rice straw (RSB) for wastewater remediation. The study is stressing the value of biochar “as a green and low-cost adsorbent [that] provides a sustainable alternative to commercial wastewater treatment technologies”, which are based on a use of chemicals usually “intensive and expensive” (Foong et al., 2022). Produced mainly by pyrolysis, biochar is modified to enhance its adsorption capacity. “Thus far, acid-modified RSB is able to remove metal ions and organic compounds, while *magnetic biochar* and electrochemical deposition have emerged as potential biochar modification techniques. Besides, temperature and pH are the two main parameters that affect the efficiency of contaminants removal by RSB” (Foong et al., 2022).

About MBC, in the review by Foong and coworkers we can find the “alkali-acid modified magnetic RSB and alkali magnetic RSB for the removal of tetracycline”, as proposed by Dai et al., 2020. The resulting adsorption capacity was much higher compared to that of the pristine RSB. An alkaline magnetic RSB was proposed for the removal of organic dye rhodamine B by Ren et al., 2020. “Chemicals and magnetic modifications can improve the surface area and enhanced the formation of oxygen-containing functional groups on the surface of RSB, thus facilitating the adsorption of target contaminants via pore-filling effects and hydrogen bonding” (Foong et al., 2022, Dai et al., 2020, Ren et al., 2020). The review by Foong and coworkers continues with the co-metal modified biochar, where the modification can increase the presence of oxygen-containing groups on RSB surface. “As a whole, post-treatment of RSB constitutes a new research area that targets to maximize the potential of the abundantly available rice straw waste as a cost-effective adsorbent” (Foong et al., 2022), to improve biochar surface chemistry and porous structure.

9. The bottleneck

Yi et al., 2020, start their review from the main bottleneck of the use of biochar, which is the “difficulty of separating the powdered biochar from the environmental medium”. This bottleneck is also hindering “the large-scale application of biochar as an adsorbent”. The strategy investigated is that of using transition metals and related oxides to obtain MBC to be applied as “adsorbent or catalyst in environmental remediation”. Besides the discussions about the adsorption of nuclear waste pollutants, of organic pollutants and of inorganic anion pollutants, we can find also information regarding combined pollutants and the catalytic degradation of organic pollutants. A section of the article by Yi et al., is also regarding the regeneration and recycling of MBC. After the adsorption of pollutants and the separation by means of a magnetic field, we have an exhausted magnetic biochar which can be reused after regeneration. “Nowadays, according to the different properties of pollutants, the common regeneration reagents include hydrochloric acid, sodium hydroxide, chelating agent, organic solvent, etc.” (Yi et al., 2020). Physical methods such as ultrasonication and oven-drying are also involved in the regeneration. However, to ensure “the reactivity of magnetic biochar after regeneration is crucial to the application of magnetic biochar” (Yi et al., 2020).

Yi and coworkers are mentioning further issues about the use of magnetic biochar. One is regarding the “environmental toxicity of magnetic biochar”, that needs to be carefully investigated. Moreover the “release of pollutants adsorbed onto magnetic biochar should be prevented and a long-term monitoring system established to prevent secondary pollution”, that is it is necessary to have a proper framework for the use of MBC for wastewater treatments. Since the pollutant substances are often present with other substances in the magnetic biochar, it is necessary to be selective in removing them. Another important issue is regarding equipment: the separation and recovery of MBC “should be realized by fully combining with magnetic separation equipment to evaluate the feasibility of its material engineering applications” (Yi et al., 2020). That is, the use of magnetic biochar is a logistic problem, which needs the same approach to other logistic problems related to environmental relevant processes.

10. Extensively applied MBC

The review by Qu et al., 2022, has an abstract starting in the following manner: “Magnetic biochar (MBC) is extensively applied on contaminants removal from environmental medium for achieving environmental-friendly remediation with reduction of secondary pollution owing to its easy recovery and separation”. As highlighted by authors, the article proposes the presentation of synthesis methods and raw materials for MBC, the discussion of adsorptive mechanisms, the advancements in MBC modifications, and some clarifications and suggestions about applications. After a detailed discussion of processes and properties, the authors conclude with further prospects, that “Although functionalized MBC is widely used in environmental remediation, there are still some factors that limit its large-scale utilization, which need to be considered in the future”. It seems that the “widely used” MBC is referring to research laboratories and, possibly, to some pilot plants, since the authors add that there are limits to a full-scale utilization. Then we are again at the same conclusions as before: costs, quantities and by-products are problems that need to be carefully considered to pass from laboratories to real-life applications.

The same conclusions we can find given by Enaime et al., 2020, in their review about biochar conversion technologies. The researchers conclude that "it is undoubted that the application of biochar offers several benefits and potential economic and environmental advantages, and *its efficiency to remove different contaminants in the lab-scale has been widely reported*. However, more in situ experiments should be performed to test the biochar efficiency using real effluents and to examine the real effect of biochar on the environment prior to its large-scale application" (Enaime et al., 2020). And also Alsawy et al., 2022, in their article about the regeneration of biochar adsorbent for wastewater treatment, tell that "many works highlighted the effectiveness of using biochar in extracting and recovering valuable metals from wastewater. However, these studies were conducted at the lab-scale level". Alsawy and coworkers suggest that more research is required to "raise the technological readiness level" of adsorption/desorption methods for the wastewater treatment by means of biochar.

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