



“Gheorghe Asachi” Technical University of Iasi, Romania



Fe(II) AND Mn(II) REMOVAL FROM CONTAMINATED GROUNDWATER BY ADSORPTION: A COMPARISON OF ACTIVATED CARBON AND PINE BARK

Silvia Sbaffoni¹, Maria Rosaria Boni², Pierpaolo Tedesco², Mentore Vaccari^{3*}

¹ENEA- Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Research Centre
Casaccia, Sustainability Department, Via Anguillarese 301, 00123 Rome, Italy

²Department of Civil and Environmental Engineering, SAPIENZA University of Rome, via Eudossiana 18, 00184 Rome, Italy

³Department of Civil Engineering, Architecture, Land, Environment and of Mathematics, University of Brescia, via Branze 43,
25123 Brescia, Italy

Abstract

This paper aims to compare the adsorption performance of activated carbon and pine bark for iron and manganese removal from contaminated groundwater. Moreover, their environmental compatibility was checked for their possible use as reactive media in a permeable reactive barrier for in situ remediation. Batch tests were carried out with different iron and manganese concentrations and different particle-size distributions, in order to evaluate the effectiveness of the activated carbon and pine bark on removal depending on both the initial pollutant concentration and the surface area of the adsorbent. High removal efficiencies were reached by both of the reactive media. However, faster removal at higher concentration was observed only for iron adsorption by activated carbon. The particle-size distribution did not significantly influence the process in the experimental conditions tested. The immobilization process on the reactive media can be considered almost irreversible since the quantities of iron and manganese released during the desorption tests were negligible.

Key words: adsorption, biosorbents, contaminated groundwater, heavy metals

Received: February, 2016; *Revised final:* June, 2016; *Accepted:* July, 2016; *Published in final edited form:* August, 2018

1. Introduction

Geological formation, waste effluents of industrial processes as well as old landfills are primarily responsible for the occurrence of iron and manganese ions in groundwater (Masukume et al., 2017; Tchobanoglous et al., 2003). Iron is usually present in groundwater as a divalent ion (Fe^{2+}), while manganese is frequently found in either its divalent (Mn^{2+}) or quadrivalent (Mn^{4+}) form (Vondráčková et al., 2017). The presence of high concentrations of these ions in groundwater causes aesthetic, organoleptic and operating problems, thus the regulation in force sets an upper limit of 200 $\mu\text{g/L}$ and

50 $\mu\text{g/L}$ for iron and manganese, respectively (Legislative Decree 152, 2006). The processes available for iron and manganese removal from groundwater are either physico-chemically or biologically based. In particular, both chemical and biological oxidation is the most widespread technology. Oxygen or stronger oxidants, such as chlorine (ClO_2) and potassium permanganate (Ellis et al., 2000; Knocke et al., 1991), are generally used in chemical oxidation (Collivignarelli et al., 2018). The solid products of oxidation ($\text{FeOOH}\cdot\text{H}_2\text{O}$ and MnO_2) are then filtered through a granular bed. However, in water treatment processes, the use of chemical reagents should be minimized, not only because of the

* Author to whom all correspondence should be addressed: e-mail: mentore.vaccari@unibs.it; Phone: +39 030 3711300; Fax: +39 030 3711213

increase in the operational costs of the applied treatment methods, but also because of secondary impacts that may arise due to residuals and by-product formation (Bertanza et al., 2018; Collivignarelli et al., 2008, 2011). For these reasons, biological oxidation has been considered as a viable alternative for groundwater clean-up. Fe and Mn removal by biological processes is generally based on different stages of biofiltration where beds are colonized by Fe–Mn oxidizing bacteria (Hope and Bott, 2004; Pacini et al., 2005; Štembal et al., 2005). In nature, iron oxidizing bacteria (IOB) and manganese oxidizing bacteria (MnOB) are widespread. These bacteria, present in raw water, can multiply in sand filters under appropriate conditions and are able to oxidize Fe(II) and Mn(II), which precipitate under their oxidized forms Fe(III) and Mn(IV) (Corstjens et al., 1992; Katsoyiannis and Zouboulis, 2004; Sjøgaard et al., 2000). IOB can be aerobic or microaerobic as a function of pH values, whereas MnOBs are strictly aerobic with oxygen concentrations higher than 5 mg/L. There are also various non-oxidative methods for iron and manganese removal from groundwater, e.g. ion-exchange (Vaaramaa and Letho, 2003; Yuca and Alptekin, 2013), adsorption (Munter et al., 2005), bioremediation and treatment with limestone (Berbenni et al., 2000) and precipitation (Das et al., 2007). Among these, adsorption on activated carbon (bin Josoh et al., 2005; Budinova et al., 2009; Dastgheib and Rockstraw, 2002; Moreno-Piraján et al., 2011; Okoniewska et al., 2007) and other adsorbent materials (Janoš et al., 2016) can be used in *ex situ* treatment plants or for *in situ* permeable barriers for groundwater clean-up.

Due to the high costs linked to the activated carbon and to the loss of efficiency in the case of dissolved inorganic and organic matter naturally present in the groundwater, the testing of low-cost materials that can guarantee good performance in pollutant removal is of great interest. Thus most studies have been focused on natural zeolites (Al-Anber M. and Al-Anber Z., 2008; Esfehiani and Shamohammadi Heidari, 2011; Shavandi et al., 2012; Varvara et al., 2013) and on low-cost non-living biosorbents and waste materials, such as bark (Acemioglu, 2004; Chockalingam and Subramanian, 2009), corn (Nassar et al., 2004), rice husk (Ghorbani and Eisazadeh, 2012; Mohan and Sreelakshmi, 2008), eggshells (Yeddou and Bensmaili, 2007), wooden charcoal (Ahamad and Jawed, 2010), and banana ash (Bordoloi et al., 2011). Low-cost biosorbent materials have been widely tested also for the removal of cadmium (Naiya et al., 2009; Nehrenheim et al., 2011; Shin et al., 2007; Tofan et al., 2012), chromium (Bhattacharya et al., 2008; Krowiak et al., 2011; Sarin and Pant, 2006), copper (Amalinei et al., 2012; Khokhotva, 2010; Khokhotva and Waara, 2010; Krowiak et al., 2011; Mohan and Sreelakshmi, 2008), lead (Khokhotva, 2010; Khokhotva and Waara, 2010; Mohan and Sreelakshmi, 2008; Nehrenheim et al., 2011), nickel (Khokhotva, 2010; Khokhotva and Waara, 2010; Nehrenheim et al., 2011; Subbaiah et al.,

2009), zinc (Khokhotva, 2010; Khokhotva and Waara, 2010; King et al., 2008; Mohan and Sreelakshmi, 2008; Naiya et al., 2009; Nehrenheim et al., 2011) and organic micro-pollutants (Antunes et al., 2012; Braga et al., 2011).

The present work aimed at testing the performance of commercially activated carbon and pine bark in the removal of Fe(II) and Mn(II) ions from aqueous solutions. The bark was chosen due to its low cost and its performances were compared to those obtained through the most traditional activated carbon. The environmental quality of both materials was assessed for their possible use as reactive media in a permeable reactive barrier. The effects of iron and manganese concentration (100, 1000 and 10000 µg/L), particle-size distribution of the reactive media on the adsorption process were examined. Moreover, adsorption kinetics, isotherm studies by means of Freundlich and Langmuir models and desorption tests were performed. Finally, also preliminary considerations on the cost analysis were carried out.

2. Material and methods

2.1. Reactive media

The granular activated carbon (GAC) used in the study was made from coconut shells by steam activation, which then produces black granules with a diameter in the range of 0.425-1.70 mm. It was developed especially for the purification of potable water, meeting the requirements of the U.S. Food Chemicals Codex (U.S.P., 2008) and the Drinking Water Standard EN 12915 (European Normalisation, 2003). It is odourless and refractory to biological degradation.

In order to check the influence of the surface area on the adsorption process, it was decided to split the GAC particles into two sub-classes having the following nominal diameters:

- 0.425 – 1 mm (namely “F”, which stands for “fine”);
- 1 – 1.7 mm (namely “C”, which stands for “coarse”).

Tests conducted with raw GAC (whose diameter is within 0.425 – 1.7 mm) are indicated with a “T”, which stands for “total”.

Raw pine bark (from Italy) was air-dried for 24 hours, grinded by knife mill, washed with demineralised-distilled water (DDW) and dried at 105°C. In order to check the influence of the surface area on the adsorption process, three different particle-size classes were used with the following nominal diameters:

- 0.425 – 1 mm (namely “F”);
- 1 – 2 mm (namely “C”);
- 0.425 – 2 mm (namely “T”).

The choice of the different grain-size ranges of pine bark was influenced by the particle-size of commercial GAC and by sub-classes chosen for this study. In order to ensure equity in the comparison between the results obtained for the two materials

tested, the aggregates of pine bark were made to fall in the same range as those of GAC. Both materials were characterised in terms of their iodine number (ASTM, 2006), which is a relative indicator of porosity and the surface area of an adsorbent material.

2.2. Contaminated solutions

Fe(II)- and Mn(II)-contaminated solutions were obtained by solubilizing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (by the Carlo Erba company, used as received), respectively in demineralised-distilled water (DDW). In order to check the influence of the initial pollutant load on the removal kinetics, three different contaminated solutions were prepared for each contaminant, with the following initial concentrations (C_0):

- 100 $\mu\text{g/L}$;
- 1,000 $\mu\text{g/L}$;
- 10,000 $\mu\text{g/L}$.

Only 1,000 and 10,000 $\mu\text{g/L}$ concentrations were tested on pine bark, due to the interferences exerted by the manganese naturally present on the reactive medium and released in the solution. The iron-contaminated solutions were used immediately after their preparation, in order to avoid the spontaneous auto-catalytic oxidation of Fe(II) into Fe(III), leading to the precipitation of ferric oxides. Moreover, a mixed solution containing both 10 mg/L of Fe(II) and 10 mg/L of Mn(II) was prepared, aimed at testing the possible competition phenomena that occurred for the adsorption sites on the reactive media.

An atomic absorption spectrometer (Perkin-Elmer 3030B) with a flame and graphite furnace atomizers was used for the iron and manganese analyses.

2.3. Batch adsorption tests

The batch tests aimed at verifying the adsorption performances of the reactive media on iron and manganese. For each batch a 100 mL glass vial was used with a liquid-to-solid ratio (L/S) equal to 10 L/kg, taking care to avoid the presence of air in order to promote the establishment of anoxic/anaerobic conditions and to limit the natural Fe(II) oxidation. Then the bottles were placed in an overhead mixer Rotax 6.8 (Velp Scientifica) at 15 rpm for periods of 0.5h, 1h, 4h, 8h, 12h, 24h and 48h, based on the results obtained by previous similar studies (Acemioglu, 2004; bin Jusoh et al., 2005). Glass vials did not interact with iron and manganese ions which were not absorbed by the walls of the bottles. The tests were conducted under natural pH conditions derived by mixing the contaminated solutions and the reactive media.

No reagent was added to the reactors to adjust the pH during the tests. Batches were conducted in duplicate and the averaged values are shown below. In addition, three blank tests (B) were carried out in order to evaluate the Fe and Mn release in DDW by activated carbon and pine bark.

At the end of each test the liquid phase was separated through filtration with cellulose acetate filters (with 0.45 μm pores). Prior to analysis, the pH was modified to acidic conditions by adding HNO_3 . The liquid phase was analysed in terms of the iron and manganese content by atomic absorption. The percentage of metals adsorbed by reactive media was calculated as (Eq. 1):

$$E(\%) = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium heavy metal concentrations ($\mu\text{g/L}$).

Due to the time-dependence of the removal process, the removal rate was calculated as follows (Eq. 2):

$$k = \frac{C_i - C_{i+1}}{C_i} \frac{1}{t_{i+1} - t_i} \quad (2)$$

where C_i and C_{i+1} are the contaminant concentrations detected in correspondence to two subsequent time intervals (t_i and t_{i+1} , respectively).

The adsorption capacity (X) of the reactive media was computed as follows and expressed as $\text{mg}_{\text{adsorbate}}/\text{g}_{\text{adsorbent}}$ (Eq. 3):

$$X = \frac{C_0 - C_e}{m} \cdot V \quad (3)$$

where C_0 is the initial concentration of adsorbate in solution (mg/L), C_e is the final equilibrium concentration of adsorbate in the solution after adsorption has occurred (mg/L), V is the volume of liquid in the reactor (L) and m is the mass of adsorbent (g).

In order to compare the results obtained in the tests, the adsorption capacity (X) was normalized for the initial contaminant concentration (C_0), (Eq. 4):

$$q = \frac{X}{C_0} \quad (4)$$

2.4. Adsorption isotherms

The theoretical adsorption capacity of the reactive media tested for Fe(II) and Mn(II) was determined by developing adsorption isotherms (European Normalisation, 2003). The quantity of adsorbate that can be taken up by an adsorbent is a function of the characteristics (solubility, molecular structure, molecular weight, polarity, etc.) and the concentration of adsorbate, as well as the temperature. In general, the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH is described through an invaluable curve called adsorption isotherm (Foo and Hameed, 2010). Adsorption isotherms were developed by exposing a given amount of adsorbate in a fixed volume of liquid (with iron and manganese

concentrations equal to 10 mg/L), to varying amounts of adsorbent material. In particular, the following L/S values were used for each contaminant and for each reactive medium with the T particle-size distribution: 5, 10, 20, 50, 100, 200 and 500 L/kg. The equilibrium in this experimental activity was set equal to 8 hours, as obtained in the batch tests.

At the end of the test period, when the equilibrium was achieved (the adsorption rate was equal to the desorption rate), the amount of the adsorbate remaining in the solution was measured.

Equations that are usually used to describe the experimental isotherm data were developed by Freundlich and Langmuir. The former fit the experimental data shown in the present work better. Thus it was derived empirically and is defined as follows (Eq. 5):

$$X = k \cdot C_e^{1/n} \quad (5)$$

where $1/n$ is the Freundlich intensity factor and k is the Freundlich capacity factor (indicating the affinity between the adsorbate and the adsorbent), expressed as $\text{mg}_{\text{adsorbate}}/\text{g}_{\text{adsorbent}} \cdot (\text{L}_{\text{solution}}/\text{mg}_{\text{adsorbate}})^{1/n}$. The constants of the Freundlich isotherm can be determined by plotting $\log X$ versus $\log C_e$ and by making use of Eq. (4) rewritten as Eq. (6):

$$\log X = \log k + \frac{1}{n} \log C_e \quad (6)$$

The tests were performed following the same procedure adopted for the batch adsorption tests.

2.5. Desorption tests

The desorption tests were carried out in order to evaluate the possible iron and manganese release from the reactive media after the adsorption process. Prior to the adsorption tests, the following adsorption tests were performed at a L/S equal to 10 L/kg:

- GAC/pine bark + DDW (blank test);
- GAC/pine bark + Fe(II) solution ($C_0 = 10$ mg/L and $C_0 = 1$ mg/L);
- GAC/pine bark + Mn(II) solution ($C_0 = 10$ mg/L and $C_0 = 1$ mg/L).

These adsorption tests lasted 48 h according to the procedures described above (batch adsorption tests). Then for the desorption tests the adsorbent medium obtained was mixed to a slightly acidic DDW (pH = 5.5), at a L/S equal to 10 L/kg. The reactors were placed in an overhead mixer Rotax 6.8 (Velp Scientifica) at 15 rpm for 24 hours.

At the end of both of the adsorption and desorption tests the liquid phase was separated through filtration with cellulose acetate filters with 0.45 μm pores. Prior to analysis the pH was corrected to acidic conditions by adding HNO_3 . The liquid phase was analysed in terms of the iron and manganese content by atomic absorption and then the following parameters were calculated:

- the adsorbed micrograms, representing the mass of contaminant adsorbed on the reactive media during the adsorption test after 48 hours. The value was calculated as follows (Eq. 7):

$$\mu\text{g}_{\text{adsorbed}} = (C_0 - C_e) \cdot \text{liters of contaminated solution used} \quad (7)$$

- the micrograms of contaminants on the adsorbent material, representing the mass of contaminant present on the reactive media undergoing the desorption test. This represented only a fraction of the reactive medium used in the adsorption test, due to the unavoidable mass loss during the separation procedure (centrifugation and filtration) (Eqs. 8, 9):

$$\mu\text{g}_{\text{on the adsorbent}} = \mu\text{g}_{\text{adsorbed}} \cdot \frac{\text{g of adsorbent in the desorption test}}{\text{g of adsorbent in the adsorption test}} \quad (8)$$

$$\mu\text{g}_{\text{desorbed}} = \text{concentration in solution} \cdot \text{liters of DDW in the desorption test} \quad (9)$$

The percentage of desorbed metals was then calculated as follows (Eq. 10):

$$\text{release}(\%) = \frac{\mu\text{g}_{\text{desorbed}}}{\mu\text{g}_{\text{on the adsorbent}}} \cdot 100 \quad (10)$$

3. Results and discussion

3.1. Iron and manganese release by GAC and pine bark

Mn release from activated carbon was always lower than 0.035 mg/L and increased over time. A higher Fe release was observed, even if below 0.18 mg/L. Its maximum concentration was observed at 4 hours, then decreasing to about 0.04 mg/L after 24 hours, probably due to the re-adsorption of the leached iron onto the GAC.

The amount of both iron and manganese released by GAC did not seem able to interfere with the adsorption tests, even when the lowest concentration of contaminants (100 $\mu\text{g}/\text{L}$) was used.

In case of pine bark, the maximum iron and manganese release was observed at 12 hours, with values of about 0.12 mg/L for both, with re-adsorption at 24 and 48 hours.

The iron and manganese released by pine bark compromised the results of the adsorption tests at $C_0 = 0.1$ mg/L. For this reason, such tests were carried out only at $C_0 = 1$ mg/L and $C_0 = 10$ mg/L.

3.2. Batch adsorption tests

3.2.1. Activated carbon

Fe(II) removal kinetic was very fast, as shown in Fig. 1a. A removal efficiency higher than 90% was reached after only 1 hour, from initial concentrations of 1 and 10 mg/L. The worst performance occurred at the lowest C_0 value (0.1 mg/L), presenting an unstable behaviour without reaching a plateau value, evidently due to the iron release and re-adsorption onto GAC.

The simultaneous presence of Mn(II) in the contaminated solution seemed to influence Fe(II) adsorption only in the short-term, probably exerting a sort of catalytic effect with an increased removal kinetic. This effect was shown also by the adsorption capacity (q) profile over time, as presented in Table 1.

The adsorption capacity for both the 10 mg/L solutions reached the maximum plateau value of $10(\text{mg}_{\text{Fe removed}} \cdot \text{L}) / (\text{kg}_{\text{carbon}} \cdot \text{mg}_{\text{Fe0}})$, after 1 hour. Similar values were reached after 24 hours for 1 mg/L. As far as the lowest concentration was concerned, oscillating values between 1.3 and 9.4 $(\text{mg}_{\text{Fe removed}} \cdot \text{L}) / (\text{kg}_{\text{carbon}} \cdot \text{mg}_{\text{Fe0}})$ were observed.

In Fig. 1b the role exerted by the grain size on Fe(II) removal is shown. The coarse fraction was characterised by a slightly lower performance in the short term with respect to the fine fraction and the T series. At 24 and 48 hours, the removal efficiencies were almost the same (about 99%) for all the series. No significant differences were observed between the F and T series during the entire experimental activity.

The Mn removal kinetics did not vary significantly with time and with the initial concentration, reaching removal efficiency near 100%, as shown in Fig. 2a. The simultaneous presence of iron in the solution did not exert significant effects on Mn adsorption. As a confirmation, the adsorption capacity normalized for C_0 (Table 1) reached the maximum plateau value of $10(\text{mg}_{\text{Mn removed}} \cdot \text{L}_{\text{solution}}) / (\text{kg}_{\text{carbon}} \cdot \text{mg}_{\text{Mn0}})$ for all the tests after only 4 hours.

This value was similar to the maximum obtained for iron. A small influence due to the grain-size was observed only in the short-term (at 30 minutes and 1 hour), when the fine fraction was the best-performing medium. Starting from a 4 hour contact time, there were no significant differences in terms of efficiency between the T, F and C series (Fig. 2b). The maximum removal rate occurred in the first 30 minutes for both iron and manganese under all the conditions tested, as shown in Fig. 3. The k values were respectively 1.1-1.6 h^{-1} and 1.9 h^{-1} for iron and manganese in the first time interval.

Negligible removal rates were observed in the period 12-24 h and 24-48 h, due to the progressive saturation of the adsorption sites and to the low residual iron and manganese concentrations in the water. During the tests, pH remained almost constant, ranging between 9.57 and 9.68, thus pH variation did not influence the adsorption process during time. The pH of the system was influenced mainly by the natural pH of activated carbon (9.8), rather than by that of the contaminated solutions (about 5).

3.2.2. Pine bark

The Fe(II) removal efficiencies for T-series are presented in Fig. 4a. They were always higher than 90% during the entire experimental activity with the worst performances at $C_0 = 1 \text{ mg/L}$. The Mn(II) presence in the mixed solution did not lead to competition for the adsorption sites.

Table 1. Activated carbon adsorption capacity ($q=X/C_0$) for iron and manganese

| Time (hours) | Iron $(\text{mg}_{\text{Fe removed}} \cdot \text{L}) / (\text{kg}_{\text{carbon}} \cdot \text{mg}_{\text{Fe0}})$ | | | Manganese $(\text{mg}_{\text{Mn removed}} \cdot \text{L}) / (\text{kg}_{\text{carbon}} \cdot \text{mg}_{\text{Mn0}})$ | | |
|--------------|--|------------------------|-------------------------|---|------------------------|-------------------------|
| | $C_0 = 0.1 \text{ mg/L}$ | $C_0 = 1 \text{ mg/L}$ | $C_0 = 10 \text{ mg/L}$ | $C_0 = 0.1 \text{ mg/L}$ | $C_0 = 1 \text{ mg/L}$ | $C_0 = 10 \text{ mg/L}$ |
| 0.5 | 5.63 | 4.18 | 8.20 | 9.72 | 9.64 | 9.33 |
| 1 | 7.64 | 9.34 | 9.17 | 9.86 | 9.74 | 9.62 |
| 4 | 9.35 | 9.51 | 9.55 | 10.0 | 9.93 | 9.92 |
| 8 | 1.28 | 7.62 | 9.81 | 10.0 | 9.94 | 9.94 |
| 12 | 6.35 | 7.21 | 9.85 | 10.0 | 9.96 | 9.95 |
| 24 | 8.14 | 9.83 | 9.84 | 9.87 | 9.96 | 9.95 |
| 48 | 2.60 | 9.56 | 9.89 | 9.89 | 9.97 | 9.97 |

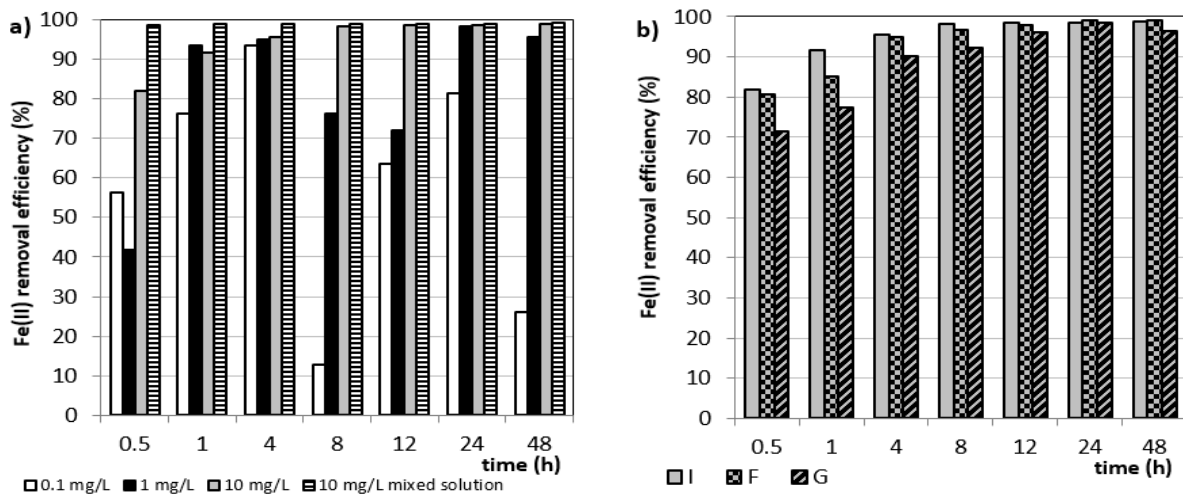


Fig. 1. Fe(II) removal efficiency by activated carbon: influence of the initial concentration for the T-series (a) and of the particle size distribution (b)

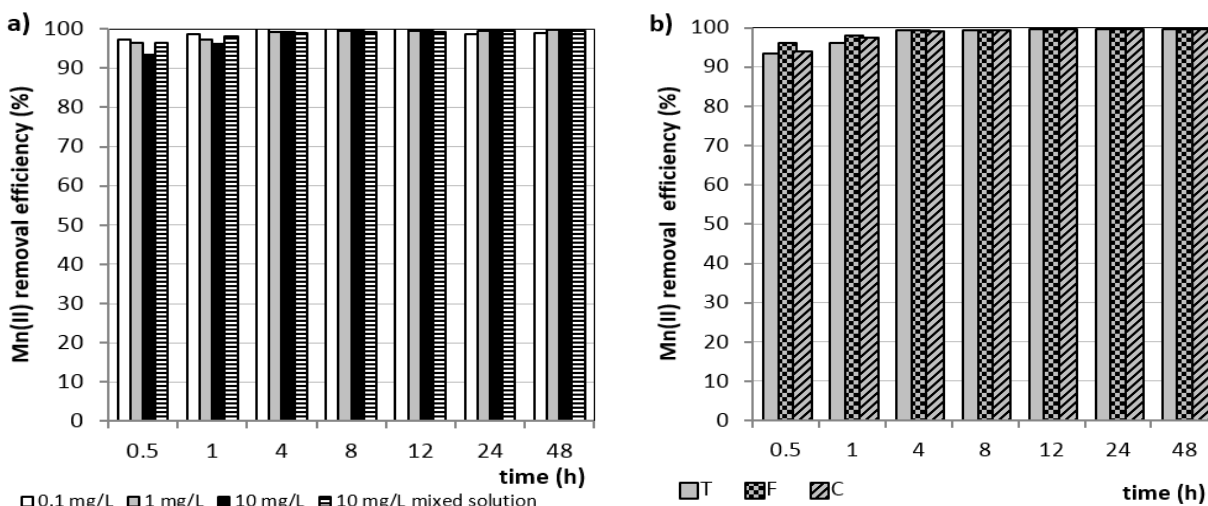


Fig. 2. Mn(II) removal efficiency by activated carbon: influence of the initial concentration for the T-series (a) and of the particle size distribution (b)

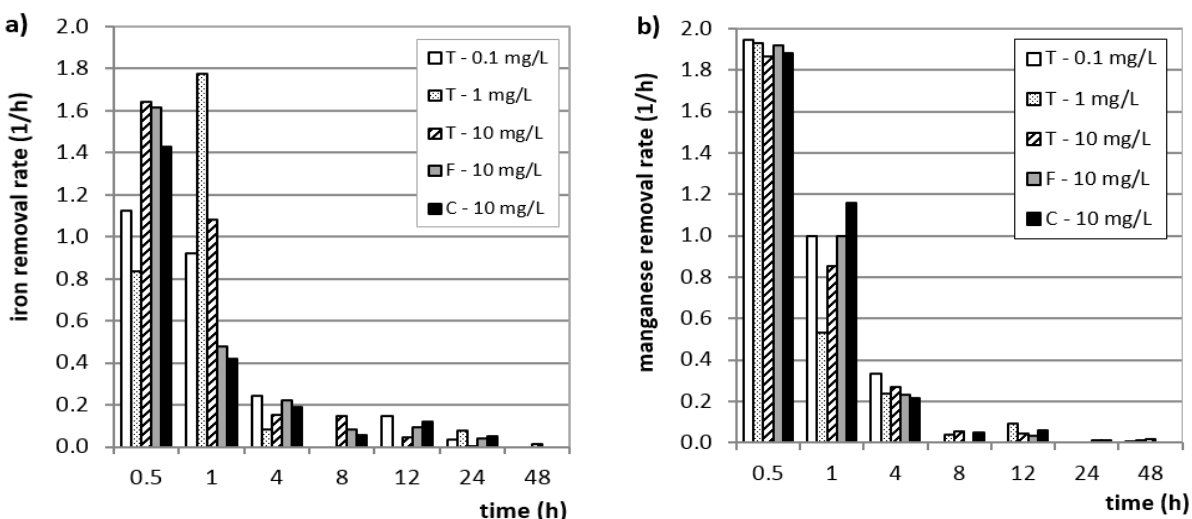


Fig. 3. Iron (a) and manganese (b) removal rates by activated carbon during the experimental activity

Iron removal efficiencies remained almost the same as those detected for the solution where only Fe(II) was present at 10 mg/L. Also the adsorption capacity (q) calculated for these two tests (only iron at 10 mg/L and mixed solution) did not vary (Table 2). It was always higher than $9 \text{ (mg}_{\text{Fe removed}} \cdot L_{\text{solution}}) / (\text{kg}_{\text{bark}} \cdot \text{mg}_{\text{Fe0}})$ and near $10 \text{ (mg}_{\text{Fe removed}} \cdot L_{\text{solution}}) / (\text{kg}_{\text{bark}} \cdot \text{mg}_{\text{Fe0}})$ for both the tests. Such values remained constant during the 48 hours.

When $C_0 = 1 \text{ mg/L}$ the adsorption capacity was always around $9 \text{ mg}_{\text{Fe removed}} \cdot L_{\text{solution}} / (\text{kg}_{\text{bark}} \cdot \text{mg}_{\text{Fe0}})$. By comparing the performance of the different grain-size classes, it can be observed (Fig. 4b) that the T-series had the highest removal efficiencies. However, in all the tests, the iron removal efficiencies were always higher than 95% after 30 minutes.

Mn removal efficiencies (Fig. 5a) registered values above 90% only when the initial concentration was 10 mg/L. At $C_0 = 1 \text{ mg/L}$ the removal efficiencies ranged between 70- 88%. The presence of iron in the contaminated solution led to a slight decrease in the manganese removal efficiencies by pine bark. However, the values were higher than 80%. The

adsorption capacity (q) was lower than that obtained for iron with mean values of $9 \text{ (mg}_{\text{Mn removed}} \cdot L_{\text{solution}}) / (\text{kg}_{\text{bark}} \cdot \text{mg}_{\text{Mn0}})$ at $C_0 = 10 \text{ mg/L}$, and $7.5 \text{ (mg}_{\text{Mn removed}} \cdot L_{\text{solution}}) / (\text{kg}_{\text{bark}} \cdot \text{mg}_{\text{Mn0}})$ at $C_0 = 1 \text{ mg/L}$ (Table 2). The performances of the different grain-size classes used in the experimental activity were quite similar, even if the removal efficiencies corresponding to the F-series were slightly lower (Fig. 5b).

The removal rates (Fig. 6) indicate that the highest values ($1.9\text{-}2 \text{ h}^{-1}$ for iron and $1.7\text{-}1.9 \text{ h}^{-1}$ for manganese) occurred in the first 30 minutes. Negligible values were calculated for manganese after 1 h and for iron after 24 h, due to the saturation of the adsorption sites as well as to the low residual Fe(II) and Mn(II) concentrations in water.

During the tests, the pH remained almost constant, with mean values ranging between 4.57 and 4.95 for iron, and 4.59 and 4.96 for manganese. Thus pH variation did not influence the adsorption process. The pH in the system was influenced by both the natural pH of bark (5.6) and that of the contaminated solutions (around 5).

3.2.3. Comparison between the reactive media performances

The findings enable comparison between the reactive media tested:

- Iron: the long-term behaviour of the two materials was similar with very similar removal efficiencies, as shown in Fig. 7a. In the short-term (up to 4 hours) pine bark was the best performing material for all the grain-size classes tested with differences of more than 10% at 30 minutes. Pine bark's removal kinetic was the fastest;
- Manganese: despite removal efficiencies higher than 90%, pine bark had lower effectiveness than

activated carbon, with differences of about 8% after 8 hours (Fig. 7b).

The adsorption capacity (X) normalized for C_0 can be considered for the comparison between the two materials. As far as iron is considered, GAC presented the maximum adsorption capacity (Fig. 8a) in the long-term. Despite the lower values obtained by pine bark, they were almost constant during the entire experimental activity. The adsorption capacity of pine bark was high even after 30 minutes. In the case of manganese, the adsorption capacity was higher as far as GAC was concerned. However, both materials produced almost constant values from 30 minutes to 48 hours (Fig. 8b).

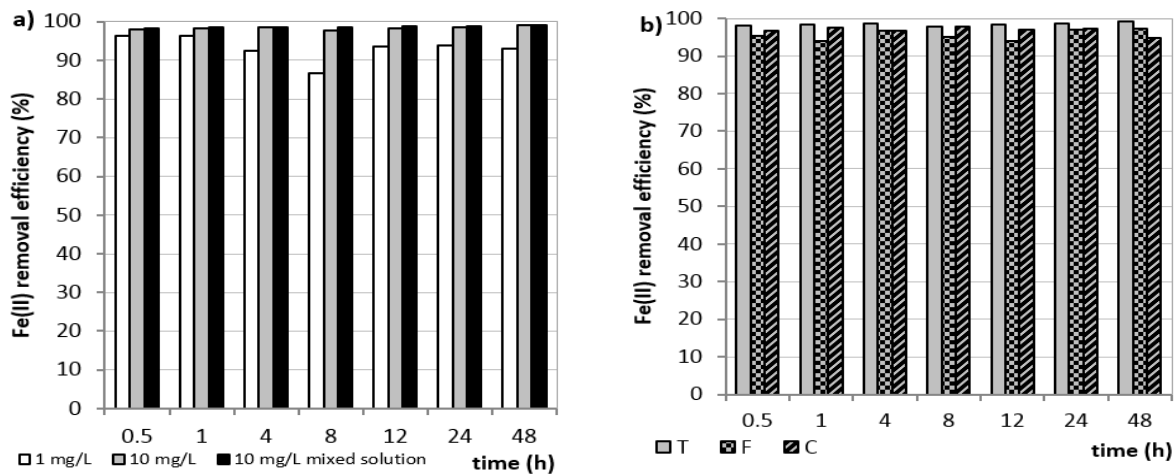


Fig. 4. Fe(II) removal efficiency by pine bark: influence of the initial concentration for the T-series (a) and of the particle size distribution (b)

Table 1. Pine bark adsorption capacity ($q=X/C_0$) for iron and manganese

| Time (hours) | Iron ($mg_{Fe} \text{ removed} \cdot L / (kg_{bark} \cdot mg_{Fe0})$) | | Manganese ($mg_{Mn} \text{ removed} \cdot L / (kg_{bark} \cdot mg_{Mn0})$) | |
|--------------|---|-------------------------|--|-------------------------|
| | $C_0 = 1 \text{ mg/L}$ | $C_0 = 10 \text{ mg/L}$ | $C_0 = 1 \text{ mg/L}$ | $C_0 = 10 \text{ mg/L}$ |
| 0.5 | 9.65 | 9.81 | 8.74 | 9.37 |
| 1 | 9.63 | 9.82 | 8.42 | 9.40 |
| 4 | 9.26 | 9.86 | 7.79 | 9.37 |
| 8 | 8.67 | 9.78 | 7.47 | 9.07 |
| 12 | 9.35 | 9.83 | 7.37 | 9.07 |
| 24 | 9.38 | 9.86 | 6.95 | 9.22 |
| 48 | 9.30 | 9.92 | 7.37 | 9.30 |

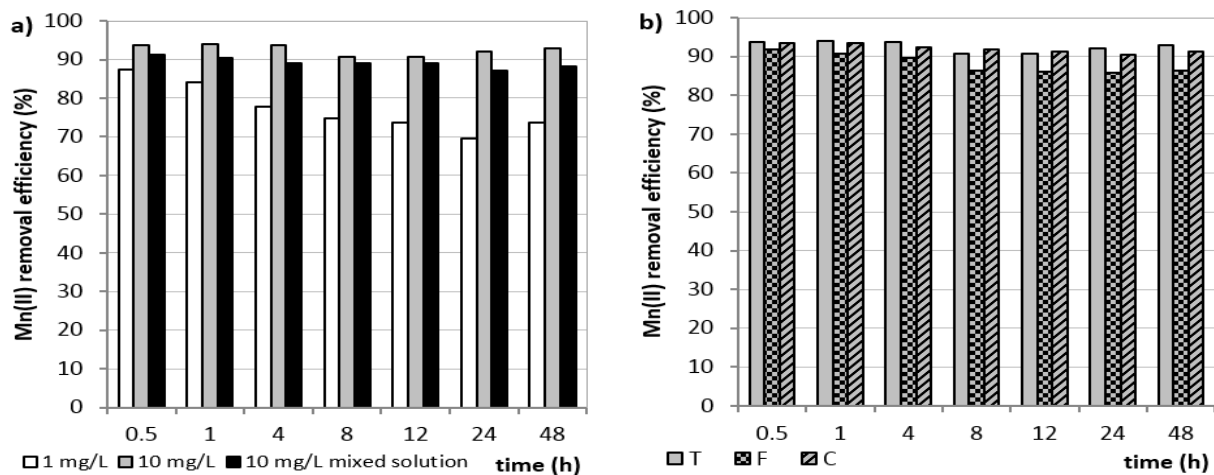


Fig. 5. Mn(II) removal efficiency by pine bark: influence of the initial concentration for the T-series (a) and of the particle size distribution (b)

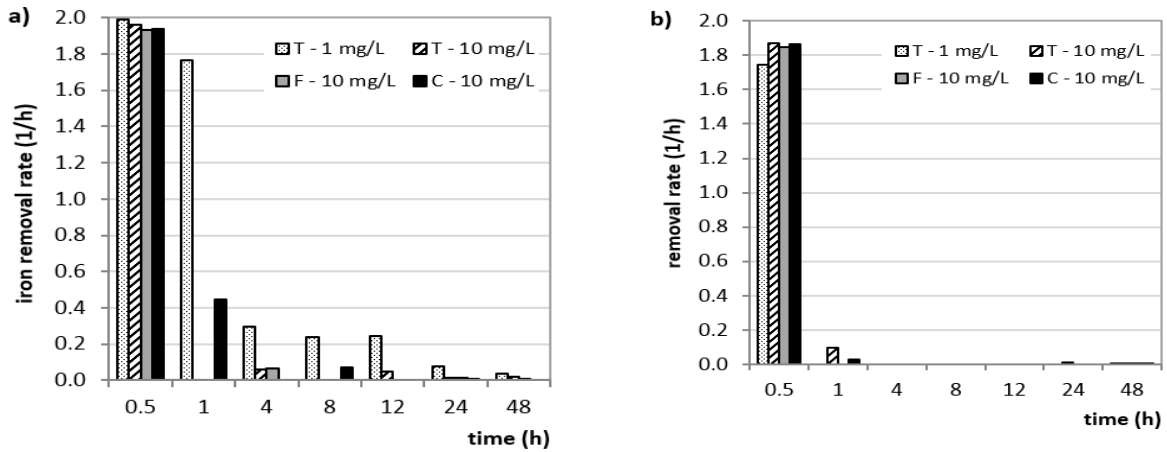


Fig. 6. Iron (a) and manganese (b) removal rates by pine bark during the experimental activity

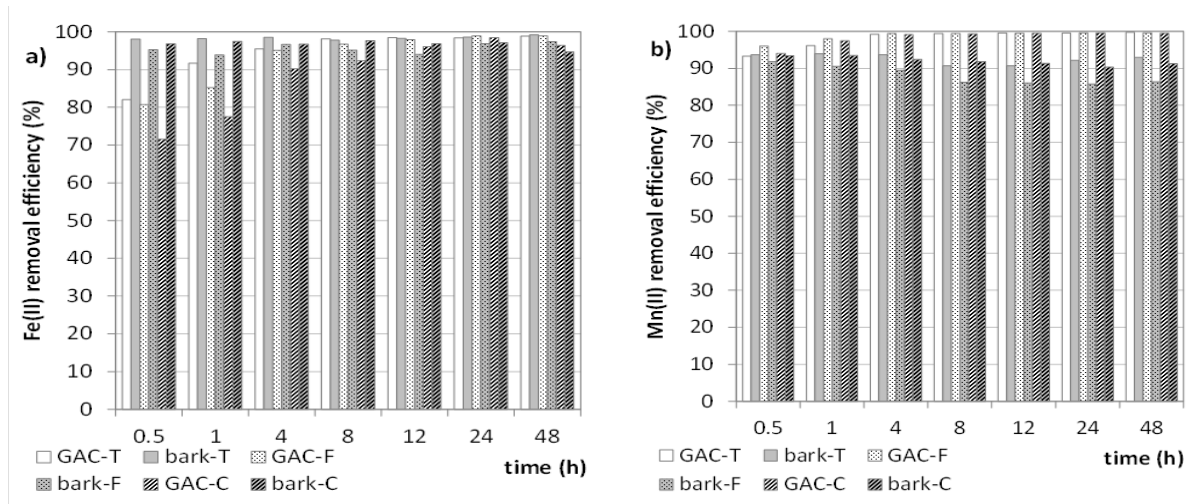


Fig. 7. Fe(II) (a) and Mn(II) (b) removal efficiency ($C_0 = 10 \text{ mg/L}$) by activated carbon and pine bark

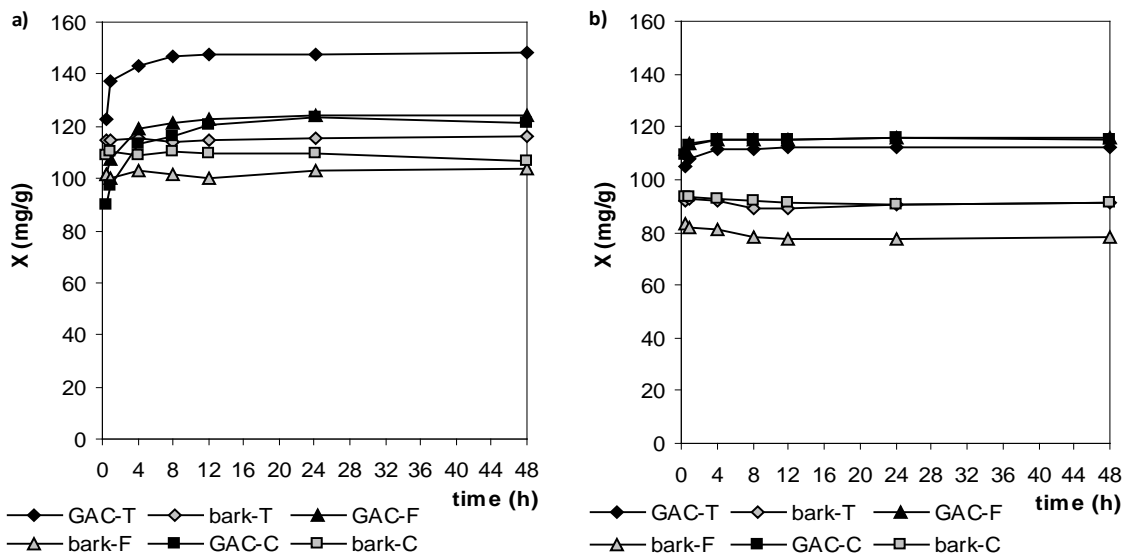


Fig. 8. Activated carbon and pine bark adsorption capacity towards iron (a) and manganese (b) with $C_0 = 10 \text{ mg/L}$

Pine bark showed good performances, although its iodine number (equal to 100) was found to be one order of magnitude lower than activated carbon (iodine number equal to 1050). This result suggests that GAC has a surface area much greater

than that of pine bark. However, any relationship between the surface area and the iodine number cannot be generalized. It varies with changes in carbon raw material, processing conditions and pore volume distribution (ASTM, 2006).

3.3. Adsorption isotherms

The data that referred to iron adsorption by activated carbon fit the Freundlich isotherm, with a correlation coefficient equal to 0.9, as shown in Table 3. On the contrary, Mn residual concentration did not depend on the quantity of adsorbent used (i.e. on the L/S value) in the range tested in the present work with values overlapping C_{eq} in correspondence to different adsorption capacity (X) values. In fact, the removal efficiency was equal to 99% in correspondence to L/S equal to 200 L/kg, remaining almost constant with higher adsorbent dosages (i.e. lower L/S). A lower removal efficiency (about 68%) was observed only in correspondence to the lowest activated carbon content (L/S = 600 L/kg). Such data confirmed the high affinity between activated carbon and manganese, as previously observed. Due to the similarity between the adsorption capacity obtained in correspondence to different L/S values, modelling through Langmuir and Freundlich adsorption isotherms was not applicable.

In the case of pine bark, the Freundlich isotherm enabled the best-fit for the experimental data, with a correlation coefficient near to 1 for both Fe and Mn (Table 3). The values of Freundlich coefficients (k and n) are shown in Table 3. The k values were very similar, confirming that pine bark had a high affinity towards both iron and manganese. Based on the low n values, it can be suggested that Mn adsorption was more dependent on the initial contaminant concentration and on the adsorbent availability, if compared to iron.

Table 2. Parameters of the Freundlich isotherm at $C_0 = 10 \text{ mg/L}$

| Parameter | GAC | | Pine bark | |
|----------------|------|----|-----------|------|
| | Fe | Mn | Fe | Mn |
| n | 1.66 | - | 1.69 | 0.79 |
| k | 4.60 | - | 2.11 | 2.29 |
| R ² | 0.90 | - | 0.98 | 0.97 |

3.4. Desorption tests

The aim of the desorption tests was to evaluate the potential release of iron and manganese ions, once adsorbed on the reactive media. The results obtained

for both activated carbon and pine bark are shown in Table 4.

The results of the desorption tests suggest that the iron and manganese released were negligible, if compared to the total quantities adsorbed on both the activated carbon and pine bark, particularly at higher pollutant concentrations. Thus, the adsorption process can be reasonably considered irreversible in the conditions tested.

3.5. Preliminary considerations on potential money savings

The GAC used cost € 470.00 per tonne, corresponding to €239.70 per cubic meter (the GAC's bulk density was equal to 510 kg/m³).

The cost of pine bark was €55.00 per cubic meter, obtained by averaging the data provided by several marketers. This value is significantly lower than that of the GAC. Thus, significant financial savings could be realised by using pine bark (about € 185.00 per cubic meter) in terms of capital investment for the set-up of the remediation action.

4. Conclusions

The experimental leads to four key conclusions, namely that:

- iron adsorption by activated carbon was influenced by the initial Fe(II) concentration. The higher the iron content, the higher the removal efficiency and the removal kinetic. The activated carbon affinity towards manganese seemed to be more evident, with kinetics not depending on the Mn(II) ions content in the contaminated solution;
- pine bark presented the highest affinity towards iron ions, with removal efficiencies higher than 97% after 30 minutes. However, despite this, its performance in manganese removal was satisfactory, with an efficiency of about 90%;
- the particle-size distribution of the reactive media and the simultaneous presence of Mn(II) and Fe(II) did not significantly influence the overall efficiencies;
- the adsorption process can be considered almost irreversible in the conditions tested, since the release obtained through the desorption tests was negligible.

Table 3. Results of the desorption tests

| | | U.M. | $C_0 = 1 \text{ mg/L}$ | | $C_0 = 10 \text{ mg/L}$ | |
|--------|--|------|------------------------|-----------|-------------------------|-----------|
| | | | Activated carbon | Pine bark | Activated carbon | Pine bark |
| Fe(II) | adsorbed | µg | 106.6 | 90.9 | 1064.8 | 962 |
| | on the adsorbent that has undergone desorption | µg | 98.9 | 58.2 | 851.1 | 604.1 |
| | desorbed | µg | - | 2.45 | 2.62 | 1.86 |
| | released | % | - | 4.21 | 0.31 | 0.31 |
| Mn(II) | adsorbed | µg | 109.5 | 670 | 1052.7 | 893 |
| | on the adsorbent that has undergone desorption | µg | 97.7 | 33.2 | 850.7 | 620.6 |
| | desorbed | µg | 0.47 | 1.98 | 1.78 | 9.73 |
| | released | % | 0.48 | 5.97 | 0.21 | 1.57 |

Based on these preliminary results, pine bark can be considered a good alternative to activated carbon as an adsorbent reactive medium, since it can ensure high performances with efficiencies comparable to those obtained with GAC (which is widely tested, but more expensive), and at lower costs. However, additional tests must be carried out in order to evaluate the durability and long-term behaviour of the pine wood for its possible use in *in situ* groundwater remediation.

Authors

Silvia Sbaffoni developed the study. She analysed and elaborated the experimental data with Mentore Vaccari and Pierpaolo Tedesco, who carried out the lab tests. Maria Rosaria Boni was the coordinator of the research.

Acknowledgements

The authors wish to thank prof. Terry Tudor for his support in English editing.

References

- Acemioglu B., (2004), Removal of Fe(II) from aqueous solution by Calabrian pine bark wastes, *Bioresource Technology*, **93**, 99-102.
- Ahamad K.U., Jawed M., (2010), Kinetics, equilibrium and breakthrough studies for Fe(II) removal by wooden charcoal: a low cost adsorbent, *Desalination*, **251**, 137-145.
- Al-Anber M., Al-Anber Z., (2008), Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron, *Desalination*, **225**, 70-81.
- Amalinei R.L.M., Miron A., Volf I., Padurarur C., Tofan L., (2012), Investigations on the feasibility of Romanian pine bark wastes conversion into a value-added sorbent for CU(II) and ZN(II) ions, *Bioresources*, **7**, 148-160.
- Antunes M.C.G., Pinto S., Braga F.G., Esteves Silva J.C.G., (2012), Optimisation of bisphenol A removal from water using chemically modified pine bark and almond shell, *Chemistry and Ecology*, **28**, 141-152.
- ASTM, (2006), Standard test method for determination of iodine number of activated carbon, ASTM D 4607-94, (2006).
- Berbenni P., Pollice A., Canziani R., Stabile L., Nobili L., (2000), Removal of iron and manganese from hydrocarbon-contaminated groundwaters, *Bioresource Technology*, **74**, 109-114.
- Bertanza G., Sorlini S., Vaccari M., (2018), Integrated Assessment Challenges in the Water, Wastewater and Waste Domains: Case Studies, *IFAC-PapersOnLine*, **51**, 25-30.
- Bhattacharya A.K., Naiya T.K., Mandal S.N., Das S.K., (2008), Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solution using different low-cost adsorbents, *Chemical Engineering Journal*, **137**, 529-541.
- Bin Jusoh A., Cheng W.H., Low W.M., Nora'aini A., Megat Mohd Noor M.J., (2005), Study on the removal of iron and manganese in groundwater by granular activated carbon, *Desalination*, **182**, 347-353.
- Bordoloi S., Nath S.K., Dutta R.K., (2011), Iron ion removal from groundwater using banana ash, carbonates and bicarbonates of Na and K, and their mixtures, *Desalination*, **281**, 190-198.
- Braga F.G., Pinto S., Antunes M.C.G., (2011), Comparative study of 17 β -estradiol removal from aqueous solutions using pine bark and almond shell as adsorbents, *Microchimica Acta*, **173**, 111-117.
- Budinova T., Savova D., Tsyntsarski B., Ania C.O., Cabal B., Parra J.B., Petrov N., (2009), Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solutions, *Applied Surface Science*, **255**, 4650-4657.
- Chockalingam E., Subramanian S., (2009), Utility of *Eucalyptus tereticornis* (Smith) bark and *Desulfotomaculum nigrificans* for the remediation of acid mine drainage, *Bioresource Technology*, **100**, 615-621.
- Collivignarelli C., Tharnpoopasiam P., Vaccari M., De Felice V., Di Bella V., Worakhunpiset V., (2008), Evaluation of drinking water treatment and quality in Takua Pa, Thailand, *Environmental Monitoring and Assessment*, **142**, 345-358.
- Collivignarelli C., Vaccari M., Vitali F., (2011), Issues and recommendations for drinking water supply in an average Bosnian town: the case study of Zavidovici, *Journal of Water Supply: Research and Technology – AQUA*, **60**, 16-26.
- Collivignarelli M.C., Vaccari M., Abbà A., Canato M., Sorlini S., (2018), Wet oxidation of fine soil contaminated with petroleum hydrocarbons: A way towards a remediation cycle, *Environments*, **5**, 1-13.
- Corstjens P.L., de Vrind J.P., Westbroek P., de Vrind-de Jong E.W., (1992), Enzymatic Fe oxidation by *Leptothrix discophora*: identification of an iron-oxidizing protein, *Applied and Environmental Microbiology*, **58**, 450-454.
- Das B., Hazarika P., Saikia G., Kalita H., Goswami D.C., Das H.B., Dube S.N., Dutta R.K., (2007), Removal of iron from groundwater by ash: a systematic study of a traditional method, *Journal of Hazardous Materials*, **141**, 834-841.
- Dastgheib S.A., Rockstraw D.A., (2002), A model for the adsorption of single metal ion solutes in aqueous solution onto activated carbon produced from pecan shells, *Carbon*, **40**, 1843-1851.
- Ellis D., Bouchard C., Lantane G., (2000), Removal of iron and manganese from groundwater by oxidation and microfiltration, *Desalination*, **130**, 255-264.
- Esfehani A., Shamohammadi Heidari Z., (2011), Manganese removal from aqueous solution by natural and sodium-modified zeolite, *Journal of Environmental Studies*, **37**, 97-104.
- European Normalisation, (2003), Products used for the treatment of water intended for human consumption – Granular activated carbon, EN 12915-1: 2003.
- Foo K.Y., Hameed B.H., (2010), Insights into the modeling of adsorption isotherm systems, *Chemical Engineering Journal*, **156**, 2-10.
- Ghorbani M., Eisazadeh H., (2012), Fixed bed column study for Zn, Cu, Fe and Mn removal from wastewater using nanometer size polypyrrole coated on rice husk ash, *Synthetic Metals*, **162**, 1429-1433.
- Hope C.K., Bott T.R., (2004), Laboratory modelling of manganese biofiltration using biofilms of *Leptothrix discophora*, *Water Research*, **38**, 1853-1861.
- Janoš P., Eletskaia A., Pilařová V., (2016), Comparison of some non-conventional sorbents for the removal of arsenic from waters, *Environmental Engineering and Management Journal*, **15**, 1721-1728.

- Katsoyiannis I.A., Zouboulis A.I., (2004), Biological treatment of Mn(II) and Fe(II) containing groundwater: kinetic considerations and product characterization, *Water Research*, **38**, 1922-1932.
- Khokhotva A.P., (2010), Adsorption of heavy metals by a sorbent based on pine bark, *Journal of Water Chemistry and Technology*, **32**, 336-340.
- Khokhotva O., Waara S., (2010), The influence of dissolved organic carbon on sorption of heavy metal on urea-treated pine bark, *Journal of Hazardous Materials*, **173**, 689-696.
- King P., Anuradha K., Lahari S.B., Kumar Y., Prasad V.S.R.K., (2008), Biosorption of zinc from aqueous solution using *Azadirachta indica* bark: equilibrium and kinetics studies, *Journal of Hazardous Materials*, **152**, 324-329.
- Knocke W.R., van Venshoten J.E., Soborsky A.W., Reckhow D.A., (1991), Kinetics of manganese and iron oxidation by potassium permanganate and chlorine dioxide, *Journal of the American Water Works Association*, **83**, 80-87.
- Krowiak A.W., Szafran R.G., Modelski S., (2011), Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, *Desalination*, **265**, 126-134.
- Legislative Decree 152, (2006), Legislative Decree 3 April 2006 n. 152, Environmental rules, Gazzetta Ufficiale n. 88, 14.04.2006, Italy (in Italian).
- Masukume M., Onyango M.S., Maree J.P., (2017), Performance characteristics of synthetic zeolite f9 in treating high iron and manganese acid mine drainage, *Environmental Engineering and Management Journal*, **16**, 2255-2265.
- Mohan S., Sreelakshmi G., (2008), Fixed bed column for heavy metal removal using phosphate treated rice husk, *Journal of Hazardous Materials*, **153**, 75-82.
- Moreno-Piraján J.C., Garcia-Cuello V.S., Giraldo L., (2011), The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells, *Adsorption*, **17**, 505-514.
- Munter R., Ojaste H., Sutt J., (2005), Complexed iron removal from groundwater, *Journal of Environmental Engineering*, **131**, 1014-1020.
- Naiya T.K., Chowdhury P., Bhattacharya A.K., Das S.K., (2009), Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions, *Chemical Engineering Journal*, **148**, 68-79.
- Nassar M.M., Ewida K.T., Ebrahiem E.E., Magdy Y.H., Mheaedi M.H., (2004), Adsorption of iron and manganese ions using low-cost materials as adsorbents, *Adsorption Science and Technology*, **22**, 25-37.
- Nehrenheim E., Odlare M., Allard B., (2011), Retention of 2,4,6-trinitrotoluene and heavy metals from industrial waste water by using the low cost adsorbent pine bark in a batch experiment, *Water Science & Technology*, **64**, 2052-2058.
- Okoniewska E., Lach J., Kacprzak M., Neczaj E., (2007), The removal of manganese, iron and ammonium nitrogen on impregnated activated carbon, *Desalination*, **206**, 251-258.
- Pacini V.A., Ingallinella A.M., Sanguinetti G., (2005), Removal of iron and manganese using biological roughing up filtration technology, *Water Research*, **39**, 4463-4475.
- Sarin V., Pant K.K., (2006), Removal of chromium from industrial waste by using eucalyptus bark, *Bioresource Technology*, **97**, 15-20.
- Shavandi M.A., Haddadian Z., Ismail M.H.S., Abdullah N., Abidin Z.Z., (2012), Removal of Fe(III), Mn(II) and Zn(II) from palm oil mill effluent (POME) by natural zeolite, *Journal of the Taiwan Institute of Chemical Engineers*, **43**, 750-759.
- Shin E.W., Karthikeyan K.G., Tshabalala M.A., (2007), Adsorption mechanism of cadmium on juniper bark and wood, *Bioresource Technology*, **98**, 588-594.
- Søgaard E., Medenwaldt R., Abraham-Peskir J.V., (2000) Conditions and rates of biotic and abiotic iron precipitation in selected Danish freshwaters plants and microscopic analysis of precipitates morphology, *Water Research*, **34**, 2675-2682.
- Štembal T., Makić M., Ribičić N., Briški F., Sipos L., (2005), Removal of ammonia, iron and manganese from groundwaters of Northern Croatia – pilot plant studies, *Process Biochemistry*, **40**, 327-335.
- Subbaiah M.V., Vijaya Y., Kumar N.S., Reddy A.S., Krishnaiah A., (2009), Biosorption of nickel from aqueous solutions by *Acacia leucocephala* bark: kinetics and equilibrium studies, *Colloids and Surfaces B*, **74**, 260-265.
- Tchobanoglous G., Burton F.L., Stensel H.D., (2003), *Wastewater Engineering: Treatment and Reuse*, Fourth Edition. Metcalf & Eddy Inc., Mc Graw Hill, New York.
- Tofan L., Paduraru C., Robu B., Miron A., Amalinei R.L.M., (2012), Removal of Cd(II) ions from aqueous solution by retention on pine bark, *Environmental Engineering and Management Journal*, **11**, 199-205.
- U.S.P., (2008), *Food Chemical Codex*, U.S. Pharmacopeial Convention, 6th Edition.
- Vaaramaa K., Letho J., (2003), Removal of metals and anions from drinking water by ion exchange, *Desalination*, **155**, 157-170.
- Varvara S., Popa M., Bostan R., Damian G., (2013), Preliminary considerations on the adsorption of heavy metals from acidic mine drainage using natural zeolite, *Journal of Environmental Protection and Ecology*, **14**, 1506-1514.
- Vondráčková S., Hejcman M., Tlustoš P., Száková J., (2017), Effect of rock phosphate and superphosphate application on mobility of elements (Cd, Zn, Pb, As, Fe, Mn) in contaminated soils, *Environmental Engineering and Management Journal*, **16**, 2901-2910.
- Yeddou N., Bensmaili A., (2007), Equilibrium and kinetic modelling of iron adsorption by eggshells in a batch system: effect of temperature, *Desalination*, **206**, 127-134.
- Yuce G., Alptekin C., (2013), In situ and laboratory treatment tests for lowering of excess manganese and iron in drinking water sourced from river-groundwater interaction, *Environmental Earth Sciences*, **70**, 2827-2837.