Removal of dissolved organic matter (DOM) from water with activated carbon and effective microorganisms

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ABSTRACT

Humic substances (HS) cause problems in water purification because of disinfection by-product (DBP) formation during chlorination. The efficiency of activated carbon (AC) adsorption as a method in drinking water treatment has been investigated in removing HS at different pH values (pH = 5; 6; 7; 8) in static equilibrium experiments. The degradation of HS was studied with an EM (effective microorganisms) bacteria community, and solutions of fulvic acid, sodium humate furthermore extracts of sandy soil were investigated. EM products are widely used but their effect on HS has not been investigated before. The combination of EM and AC methods in the case of fulvic acid resulted in higher performance than any of these methods alone. Humic substances were analyzed using a UV–VIS spectrophotometer and by total organic carbon (TOC) measurements. The carbon/nitrogen ratio was also determined, which enabled conclusions to be made for the nutrient supply. According to these results the degradation was efficient, especially in fulvic acid solutions.

Key words | adsorption, biological degradation, drinking water, GAC, humic substances

INTRODUCTION

Adsorption is an important process in drinking water as well as waste water treatment. The affinity between the solute and the adsorbent can be characterized by adsorption isotherms generated in static equilibrium experiments.

Isotherms of organic solutes were divided into four main groups by Giles et al. (1960). The basis of this classification is the initial slope of their curve. The S-type isotherms indicate e.g. a strong competition between the solute and solvent molecules for substrate sites, while the L (‘Langmuir’) curve characterizes the case that the solute has a high affinity for the adsorbent. The H curve means very strong interaction between the solute and the adsorbent. In C-type isotherms, linear relationships can be observed with constant partition when the availability of sites remains constant at every concentration value up to saturation.

The above classification of adsorption isotherms can also be used in the removal of humic substances from water by activated carbon. The adsorption performance can be improved by using small-size granulated activated carbon (GAC), low pH, low temperature, and a significant increase in the dosage of GAC (Chen et al. 1996).

Activated carbon is the most effective in combined processes (Kim & Yu 2007; Lin et al. 2005), for instance in ozonization and AC (Janssens et al. 1985; Okawa et al. 2004), and in coagulation and AC (Yuasa 1998; Uygunera et al. 2007; Kalderisa et al. 2008; Zhao et al. 2008). Biofiltration with GAC is also effective (Kooij et al. 1989; Kong et al. 2000), however, it is not widely applied in removal of precursors of disinfection by-products (DBPs) (Vahala et al. 1999).

According to Bouwer & Crowe (1988), biological processes are able to remove pollutants that may be ineffectively removed by conventional treatments, like biodegradable organics, synthetic organic compounds and some inorganic substances. Biooxidation of organic matter and ammonia decreases available substrates for microbial regrowth in distribution systems. Furthermore, it reduces tastes and odours, and decreases the amount of precursors available to form DBPs. Practical experience in Europe...
with media containing microbial activity has been favorable. The efficiency of biological GAC filtration strongly depends on temperature (Servais et al. 1992). Zhao et al. (2008) did not find a direct relation between the amount of biomass or the thickness of the biofilm on the carbon and the remaining adsorptive capacity. According to Graham (1999) and Janssens et al. (1985) preozonization produces oxygenated organic byproducts that are more readily biodegradable, which makes biological filtration processes more effective. Ozonization prior to biological GAC filtration resulted in a final water quality generally with lower organic matter concentration (Janssens et al. 1985). Biofilm contact oxidation also has an excellent effect on removing ammonium nitrogen from water (Hattori 1988).

‘Effective microorganisms’ (EM) consist of lactic acid bacteria, photosynthetic bacteria and nitrogen-fixing bacteria. EM products contain Bacillus subtilis var. notto, Bifidobacterium animalis ssp. lactis, Bifidobacterium bifidum, Bifidobacterium longum, Lactobacillus acidophilus, Lactobacillus buchneri, Lactobacillus bulgaricus, Lactobacillus casei, Lactobacillus plantarum, Lactococcus diacetylactis, Lactococcus lactis, Rhodopseudomonas palustris, Rhodopseudomonas sphaeroides, Saccharomyces cerevisiae, Streptococcus thermophilus microorganisms (Greenman Ltd. 2011). Aerobic and anaerobic species live together in an anaerobic environment supporting each other. The bacteria were isolated from nature, they are not harmful, and their use has been found to be efficient as well as safe in different areas. The EM mixture is applied for instance in agriculture, waste management, waste water treatment and remediation, protecting natural waters. They degrade and transform organic materials into easily available nutrients for plants. EMs roll back pathogen microbes, and produce numerous bioactive compounds like organic acids, antioxidants, enzymes and vitamins (Hoshino et al. 2002; Ryang et al. 2002).

HS causes one of the main problems of water treatment because of DBPs formation during chlorination (Singer 1999; Lou et al. 2010). EM products are widely used in different areas, however, their effect on HS has not been investigated yet.

Our aim was to study the efficiency of HS removal from water by GAC, to investigate the effect of EM on degradation of dissolved organic matter (DOM), and furthermore to examine the combination of EM and GAC in removing DOM.

**MATERIALS AND METHODS**

**Materials**

Chemicals used in the preparation of buffer solutions (sodium dihydrogen phosphate and disodium hydrogen phosphate) were obtained from Reanal Chemical Co. (Hungary).

Sodium humate (HANa) was obtained from Roth & Co, Karlsruhe while fulvic acid (FA) was purchased by Organit Ltd. The granulated activated carbon (GAC) named FILTRASORB 400 (specific surface area is 1,050 m²/g) was provided by the firm Chemviron Carbon. An air-dry sandy soil sample (ø 0.5 mm) originated from Dabrony, Hungary was obtained and pre-treated by the Plant Health Conservation Station of Budapest. The EM bacteria community was provided by Greenman Ltd.

**The preparation of HS solutions**

100 mg L⁻¹ fulvic acid (FA) and sodium humate (HANa) solutions were made by distilled water and 0.01 mol L⁻¹ phosphate buffer at pH = 5; 6; 7; and 8.

**Adsorption experiments**

Granulated activated carbon (GAC) was applied to remove different kinds of HS and it was used in static equilibrium experiments at different pH values (pH = 5; 6; 7; 8) and in distilled water. The pH was adjusted by 0.01 mol L⁻¹ phosphate-buffer solution. 2 g GAC was added by 20 mL solution of fulvic acid (100 mg L⁻¹) or sodium humate (100 mg L⁻¹). All samples were in triplicate, and adsorption isotherms were calculated. The equilibrium concentration was determined by UV–VIS photometry (see *Analytical methods*), and the specific adsorbed amount was calculated by the following equation:

\[
q = \frac{(c_0 - c) \cdot V}{m}
\]
where $q$ is the specific adsorbed amount of solute (mg/g), $V$ is the volume of the equilibrium solution (L), $c_0$ is the initial and $c$ is the equilibrium concentration of the measuring agent (mg L$^{-1}$) and $m$ is the weighed amount of the adsorbent (g). The specific adsorbed amount was illustrated on an isotherm depending on the equilibrium concentration of the agent. Curves were fitted by the multi-step isotherm equation published by Czinkota et al. (2002).

### The degradation of DOM with EM

The degradation of humic materials was analyzed by an EM bacteria community after 1 and 7 days. Solutions of fulvic acid, sodium humate and extracts of sandy soil were investigated in 0.01 mol L$^{-1}$ phosphate buffer at pH = 7. Experiments were carried out with and without EM. The bacteria suspension was applied in 1:100 dilution ratio. Ten grams of sandy soil was shaken with 100 mL of solution for one hour and left to stand overnight for equilibration at 25°C. Equilibrium phases were separated by filtration – paper or membrane (pore size: 0.45 μm) – and were analyzed for organic carbon and total nitrogen content. EM was added to the extract before filtration and in case of another sample after filtration. All samples were in triplicate. The degradation in the liquid phase was followed by UV–VIS and total carbon/total organic carbon (TC/TOC) measurements (see Analytical methods). In order to check the nutrient supply, the total nitrogen (TN) content was also determined and the C/N ratio was calculated as the ratio of TOC (mg L$^{-1}$) and TN (mg L$^{-1}$).

### Combined method

GAC with EM as a combined method was also evaluated at pH = 7 in removing fulvic acid and sodium humate from water (100 mg L$^{-1}$ HS) after 1 and 7 days. Static equilibrium experiments were carried out after 2 g GAC was added by 0.02 mL bacteria mixture.

### Analytical methods

Fulvic acid, sodium humate concentrations and DOM content were determined in the liquid phase by a Jasco V530 UV-VIS spectrophotometer at $\lambda = 254$ nm. Standard solutions used for the analytical calibration curve of HS (FA, HANa) were prepared by exact weighing. DOM content of sandy soil extract was followed by the change of absorption at 254 nm. TC/TOC and TN was measured by Thermo Euroglas TOC 1200 equipment.

### RESULTS AND DISCUSSION

The term ‘water treatment’ is not specific because it includes methods of drinking and wastewater purification, which can also be applied in the remediation of contaminated groundwater. The present paper is a general study focusing on the removal of DOM from different aquatic systems where not only the activated carbon but even microorganisms can be used in the treatment.

### Adsorption by GAC

The pH dependency of the HS adsorption on the studied GAC sample can be seen in Figure 1(a) and (b). Fulvic acid at pH = 7 and pH = 8 resulted in an S-type isotherm indicating low affinity between the solute and the adsorbent. An L-type isotherm generated at lower pH values suggested stronger adsorption, which is mostly emphasized at pH = 5. Fulvic acid is a relatively small hydrophilic molecule, which adsorbs on GAC with high affinity (Figure 1(a)).

Humic acid is insoluble at low pH values but, dependent on the environmental conditions, it may be solubilized or even dissolved. Sodium humate, which is a soluble form of HA, was used in the experiments. This compound being salt adsorbs on GAC with lower affinity because it resulted in an S-type isotherm at all pH values investigated (Figure 1(b)) but the specific adsorbed amount was very similar to that of FA in every case.

### The degradation of DOM by EM

The degradation of humic substances by the applied bacteria community was quite efficient (Figure 2a and (b), Table 1). The most significant effect was found in the fulvic acid solution and in one of the extracts of sandy soil with membrane filtration.
Figure 1 | (a) Isotherms of fulvic acid on GAC at different pH values, (b) Isotherms of sodium humate on GAC at different pH values.

Figure 2 | (a) TOC of fulvic acid, sodium humate with EM and soil extract (made with buffer and treated with EM) after 0.45 μm filtration. (b) Absorbance at 254 nm of soil extract (made with buffer and treated with EM) after 0.45 μm filtration. Abbreviations: FA: 0.1 mol L⁻¹ fulvic acid in 0.01 mol L⁻¹ phosphate-buffer, pH = 7; EM: applied bacterium community in 1:100 dilution; B: 0.01 mol L⁻¹ phosphate-buffer, pH = 7; S: sandy soil; m: membrane filtration was applied.
In the case of fulvic acid, the TOC value slightly increased during the 1st day; at the end of the experiments (7th day) FA degraded totally (FA + EM).

Regarding sodium humate, the amount of the humic material hardly changed within the investigated period (Figure 2(a)). Sandy soil extracts were filtered by a 0.45 \( \mu \)m membrane. When the extract was made with a phosphate buffer and treated with bacteria the total degradation of organic substances could be observed (‘S + B EM m’ in Figure 2(a)). When EM was added to the soil DOM after membrane filtration, the total organic content decreased fast (‘S + B m EM’ in Figure 2(a)). Some differences in the tendency of UV absorbance and TOC values (Figure 2(a) and (b)) can be explained by various processes having different reaction rates and resulting in various degradation by-products. Non-aromatic groups could be degraded at the beginning, and might be followed by the decomposition of aromatic groups.

The change of the C/N nutrient ratio during the biodegradation test is shown in Table 1. High concentration of nitrogen could be measured in case of the fulvic acid solution and the most efficient degradation was also found in this sample.

A large C/N ratio means less N for bacteria which may hinder the degradation. The ratio was better in soil extracts than in solutions of fulvic acid or sodium humate. The C/N ratio increased in the case of sodium humate which means a lack of nutrients available for bacteria and it may lead to the experienced lower efficiency. The smaller fulvic acid is more accessible for the microorganisms than the bigger sodium humate.

**Combined application of GAC and EM**

Based on UV absorbance results GAC was effective in removing humic materials: 83% for FA and 92% for HANa. EM in themselves proved to be inefficient after one day, because the removal was only 1.3% for FA and 0.5% for HANa. When EM was applied on GAC in static equilibrium experiments, this combined method resulted in better removal than any of these methods alone: the efficiency was 97% for FA and 94% for HANa.

In the presence of bacteria (Figure 3) at pH = 7, sodium humate resulted in S-type and fulvic acid in L-type isotherms on GAC. Comparing these isotherms with the GAC experiments without EM at pH = 7 (Figure 1(a)), significant differences can be found for FA: by combining GAC with EM, higher amounts could be removed. Not only fulvic acid but also the bacteria can be bound on the activated carbon surface where the possibility of degradation is high. On the other hand, EM did not enhance the removal of sodium humate (Figures 1(b) and 3), which is a much less accessible organic compound for microorganisms.

The application of activated carbon can adsorb not only the HS but also the EM. In this case the microorganisms and

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Change of the C/N nutrient ratio during the biodegradation test</th>
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<tbody>
<tr>
<td>Time (day):</td>
<td>0</td>
</tr>
<tr>
<td>Type of humic substances</td>
<td>C/N ratio</td>
</tr>
<tr>
<td>Fulvic acid</td>
<td>40.92</td>
</tr>
<tr>
<td>Sodium humate</td>
<td>35.29</td>
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<tr>
<td>Soil susp. + (buffer with EM) membrane filtration</td>
<td>15.08</td>
</tr>
<tr>
<td>Soil susp. + (buffer with EM) from flask</td>
<td>15.08</td>
</tr>
<tr>
<td>Soil susp. with buffer, membrane filtration + EM</td>
<td>13.64</td>
</tr>
<tr>
<td>Soil susp. with buffer, paper filtration + EM</td>
<td>9.86</td>
</tr>
<tr>
<td>Soil susp. + (buffer with EM) paper filtration</td>
<td>10.99</td>
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</table>

**Figure 3** | Isotherms of fulvic acid and sodium humate at pH = 7 on GAC in the presence of EM.
the substrate (HS) are bound together to the surface and the degradation can take place more effectively.

CONCLUSIONS

Humic substances removal by AC was found efficient; however, it depended on pH value and the type and form of humic materials. FA resulted in an L-type of isotherm in slightly acidic medium indicating high affinity between the solute and the adsorbent. FA at pH = 7 and pH = 8 resulted in an S-type of isotherm indicating low affinity between the solute and the adsorbent. HANa adsorbs on GAC with lower affinity (S-type of isotherm) at all pH values investigated but the specific adsorbed amount is very similar to that of FA in every case. Degradation of humic substances by the applied bacteria community was also efficient, especially in the fulvic acid solution and in one of the extracts of sandy soil with membrane filtration. The combined EM and GAC method in static equilibrium experiments resulted in higher performance than any of these methods alone in the case of FA. The efficiency was 97% for FA and 94% for HANa. EM did not help in removing sodium humate because it is less accessible for microorganisms than the smaller fulvic acid. As there are strict regulations about using bacteria in drinking water, EM did not help in removing sodium humate because it is less accessible for microorganisms than the smaller fulvic acid. The EM did not help in removing sodium humate because it is less accessible for microorganisms than the smaller fulvic acid. As there are strict regulations about using bacteria in drinking water treatment processes they could be used for instance in the purification of contaminated water (e.g. groundwater or waste water).

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Attila Nagy (Chemviron Carbon), Erzsébet Bárdos (University of Pannonia) and Greenman Ltd for their assistance in the realization of this work.

REFERENCES


First received 16 May 2011; accepted in revised form 7 November 2011