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INTERACTIONS AND REMOVAL OF HUMIC SUBSTANCES AND DICLOFENAC FROM WATER BY ACTIVATED CARBON ADSORPTION AND MICROORGANISMS

PhD Thesis

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Abstract

One of the main problems of drinking water treatment, when the used raw water is surface water or groundwater, is presented by the dissolved organic matter (humic substances, organic micropollutants, medicines). During the chlorination process harmful disinfection byproducts may be formed. Therefore removal of dissolved organic matter must be solved effectively, for which purpose activated carbon adsorption is a widely used method. The efficiency of removal is influenced not only by the applied technology, but the stability of solution, the interactions of the dissolved substances and microorganisms presented in water.

Dissolution of humic substances from sandy soil was examined by three familiar surfactants. The particle size distribution, stability by determining zeta-potential and the adsorpion of sodium dodecyl sulphate (SDS) on sandy soil were followed. Two method, namely activated carbon adsorption and microbiological degradation with "Effective Microorganisms" and their combination were evaluated in the removal of humic substances, i.e. fulvic acid, sodium humate, humic substances dissolved from sandy soil, and of diclofenac. The mechanisms of adsorption process, chlorination of the mentioned organic substances, degradation and chlorination of the diclofenac, as well as the interaction of diclofenac with the humic acid were investigated, too.

The surfactants influence the particle size distribution of the sandy soil and mobility of smaller particles. The anionic surfactants dissolved more clorinable organic matter from the sandy soil than the cationic tenzide. SDS adsorption formed L-type isotherm, resulted in more layers, and was followed by changes in particle size distribution.

The chlorination of diclofenac may be catalyzed by clays and humic substances. Diclofenac and humic substances can be removed effectively by activated carbon, and the presence of humic substances facilitated the adsorption of diclofenac. Fulvic acid and humic substances from sandy soil were partly degraded by the applied microorganisms, while sodium-humate resisted and diclofenac has degraded especially slowly. Efficiency of the removal of humic substances has been improved when the activated carbon adsorption and the microbial degradation was jointly applied.

Introduction

Considering any region of our environment (atmosphere, hydrosphere, phedosphere) we inevitably meet the presence and role of humic substances. In the past decades, the selection of topics in national and international research also indicates that studying the origin of humic substances, examining their physico-chemical properties, clarifying their biological role, and analyzing their role in environmental transport of toxic substances represents an important direction in environmental research. Drinking water is one of the greatest treasures of mankind, providing it in sufficient quantity and quality is becoming more and more problematic for the growing population around the world, so research into possible ways of water treatment is high priority.

Organic substances dissolved in water such as humic substances and organic micropollutants (e.g. pharmaceutical and pesticide active substances) can be chlorinated during water treatment process and can be converted to such hazardous substances as trihalomethanes, chlorinated phenol derivatives known to have carcinogenic effects. 201/2001 (X. 25.) Government decree on Quality Requirements for Drinking Water and the Order of Control stated 50 mg / L as the limit value for all trihalomethanes in drinking water. Recently pharmaceutical active substances are also detected in surface raw waters, one of which is the most commonly used anti-inflammatory and analgesic agent diclofenac that remains in nature for a long time. During water purification, reacting with the disinfectant it can also form chlorination by-products.

It follows from the foregoing that the removal of the dissolved organic substances from the raw water before disinfection is high priority. The efficiency of the removal is influenced not only by the applied technological methods, but also by the stability of the solution and the interaction of the solutes in water. It is therefore worth examining these three phenomena together.

Detergents are used to dissolve substances which are none or can hardly soluble in water to form stable colloids, which can greatly influence the dissolution of humic substances. As they are widely used in different areas there are several ways for these to get into the ground and surface waters. For this reason, I found it important to examine the effect of three widely used tensids (sodium dodecyl sulfate, Cetrimide and Supragil WP) on the dissolution of humic substances from soil. Humic substances released from soil may appear both in

surface water and in groundwater used as drinking water resources, therefore special attention should be paid to their removal during water purification.

Activated carbon adsorption is often used to remove the organic water pollutants, especially when the water resource is surface water or groundwater, since these water bases contain higher amount of humic substances and organic pollutants than other raw waters. The increase of water pollutants is a continually serious problem, which is why activated carbon adsorption of water-soluble substances is continuously a current issue. Therefore, it is important to examine the effectiveness of this method on the removal of the various humic substances and diclofenac from water.

The "Effective Microorganisms" (EM) microorganism mixture, available on the market, is widely used in the agriculture, waste management and sewage treatment for various purposes due to its beneficial properties. According to the literature, the microorganisms facilitate the absorption of nutrients in the soil for plants and they are also suitable for preserving the state of the natural waters. They probably have an impact on the organic substances I have selected for testing, therefore the examination of their effect on humic substances and on diclofenac was important, including their contribution to possible degradation.

I studied the removal of humic substances dissolved in water, such as fulvic acid, sodium humate, soil extracts and diclofenac, and then I compared the effectiveness of activated carbon adsorption and microbial degradation. For this purpose, I used the methods separately and in combination. In order to understand the processes, I also studied the interaction between diclofenac and humic acid.

Theses

1. I have proved that anionic surfactants, sodium dodecyl sulphate (SDS) and Supragil WP can be a major problem in dissolving chlorinable organic matter from sandy soil compared to cationic cetyltrimethylammonium bromide (CTAB).
    a) By means of laser diffraction measurements, I ascertained that surfactants may affect the particle size distribution of soil extracts and reduce the size of particles significantly. Anionic surfactants of SDS and Supragil WP, as well as the NaCl facilitate the dispersion of smaller particles, but in the presence of electrolyte, the formation of associates is more powerful.

b) The surfactants studied enhance the formation of aggregates and flocculation in the absence of organic substances and in the presence of salt.

2. On sandy soil, the adsorption of sodium dodecyl sulphate can be characterised with three steps, resulting in an L-type (Langmuir) of isotherm, based on the initial phase of the function. I have proved that several parameters of the system with an initial cc. of 100 mg/L SDS containing also calcium ions were altered significantly. If the equilibrium concentration exceeds 32.7 mg/L, the specific adsorbed amount of SDS on the sandy soil, as well as the particle size in the soil extract increase significantly. The adsorption of SDS on sandy soil is primarily driven by hydrophobic interaction, but the presence of calcium ions may affects the process.
3. Activated carbon adsorption is effective in the removal of humic substances, but its effectiveness depends on both the type of humic substances and pH in the range of 5-8. In a weak acidic medium, fulvic acid bounds strongly to activated carbon according to the L-type isotherms, while the S-type isotherms indicate a lower affinity at pH 7 and pH 8. Sodium humate in low concentraion adsorbs on activated carbon with lower affinity resulting in S-type isotherms; but with its increasing concentration, the specific adsorbed amount is highly similar to that observed in the case of fulvic acid.
4. I have demonstrated that 'Effective Microorganisms' degraded fulvic acid and dissolved humic substances from the sandy soil in a highly affective way. The biotic removal of sodium humate — a less accessible substance for microorganisms — was less effective; due to also the decreasing nutrient content indicated by the C/N ratios.
    a) The combination of the granular activated carbon and the applied microbial process enhances the degradation of both the fulvic acid and the sodium humate compared to the single use of these approaches.
    b) 'Effective Microorganisms' break down organic matter slower than the time required for settled balance in adsorption on activated carbon. The degradation time of humic substances is few days, while it is several months for diclofenac.
5. The degradation of diclofenac in aqueous solution with humic substances is only significant in the soil extract, which may indicate the catalytic activity of clay minerals, or the enzymatic activity of microorganisms being present eventually. Removal of diclofenac by Effective Microorganisms is an especially difficult and slow process. I have proved that in the presence of humic substances, microorganisms degrade humic substances first, and only then drug substances.

6. I have shown experimentally that fulvic acid, sodium humate, humic substances released from sandy soil as well as diclofenac are all halogenated easily by chlorine; meanwhile chlorination by-products are formed.
    a) Both the fulvic acid and the sodium humate tested react similarly to chlorine. The halogenation of diclofenac is enhanced the most in the absence of further dissolved organic substances that could also be chlorinated.
    b) The chlorination of diclofenac leads also to its oxidization, but this latter process is much slower. Photocatalytic effect of humic substances in the oxidation step can also be supposed.
7. I have proved that humic substances enhances the adsorption of diclofenac on activated carbon through the interaction between diclofenac and humic substances.

Publications

Publications in referred international journals with impact factor in English

1. Rita Földényi, Szilvia Joó, Judit Tóth (2017): Adsorption of diclofenac on activated carbon and its hypochlorination in the presence of dissolved organic matter; International Journal of Environmental Science and Technology, 2017, 14(5), pp 1071–1080. doi:10.1007/s13762-016-1218-6. Impact Factor: 2.344
2. Szilvia Joó, Judit Tóth, Rita Földényi (2015): Characterization of salt- and surfactant-containing sandy soil extracts by laser light methods, International Agrophysics, 2015, 29, 291-298. Impact Factor: 1.067
3. Szilvia Joó, Rita Földényi (2012): Removal of dissolved organic matter (DOM) from water with activated carbon and Effective Microorganisms, Water Science and Technology: Water Supply, 12(1), 65-70., 2012. Impact Factor: 0.394

Publication in referred international journals in English

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1. Joó Sz., Tóth J., Samu, Gy., Földényi R.: Investigation of humic substances by particle size distribution of soils and by determination of zeta potential, *Proceedings of the XV. Meeting of International Humic Substances Society*, Tenerife, Spain, 27 June - 2 July 2010, Vol. 3. pp.108-111. Poster presentation.

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3. Joó Sz., Földényi R.: Speciális baktériumkeverék hatása a talaj vízoldható szervesanyag-tartalmára - A tápanyagok arányának követése, *XXXII. Kémiai Előadói Napok Kiadványa,* Szeged, 2009. 10. 26-28., 147-151. o. Oral presentation.
4. Joó Sz., Földényi R.: A talaj szervesanyag-tartalmának lebonthatósági vizsgálata speciális baktériumkeverék hatására rövid tartamú kísérletek során, *Proc. of the 16th Symposium on Analytical and Environmental Problems*, Szeged, 2009. 09. 28., pp 501-505. Oral presentation.
5. Joó Sz., Tóth J., Földényi R.: Humuszanyagok vizekbe jutásának körülményei és eltávolításuk aktív szenes adszorpcióval, *Proc. of the 15th Symposium on Analytical and Environmental Problems*, Szeged, 2008. 09. 22., pp 433-436. Poster presentation.
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7. Joó Sz., Tóth J., Földényi R.: Talajok szemcseméret eloszlásának vizsgálata különböző közegekben, *XXX. Kémiai Előadói Napok Kiadványa,* Szeged, 2007. 10. 29-31., pp. 131-135. Oral presentation.

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5. Joó Sz., Tóth J., Földényi R.: Humuszanyagok vizekbe jutásának körülményei és eltávolításuk aktív szenes adszorpcióval, *IHSS Magyar Tagozatának ülése*, Debreceni Egyetem AMTC, Karcagi Kutató Intézet, Karcag, 2008. 10. 30., Poster presentation.