University of Pannonia

Doctoral School of Chemical and Material Science

STUDY OF THE SORPTION PROPERTIES OF ALGINITE TO REMOVE ORGANIC CONTAMINANTS

Theses of the doctoral (PhD) dissertation

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Introduction and aim of research

As a result of different agricultural and industrial activities several micro pollutants gets into the environment. The environmental pollution is a key topic of national and international research, therefore, the purification of the contaminated natural elements requires rapid development. For the development of remediation technology, it is important to know the role of alginite in binding a pollutant. Sorption experiments were carried out to clarify the mechanism of this process.

The aim of my research was to study the innovative, environmental usability of alginite mined in Hungary, to develop the basis of a new adsorption remediation process based on the favorable properties of alginite. One of the main goals of my work was to investigate the properties of alginite that can influence the experimental processes (environmental parameters, the role of organic and mineral fractions of alginite). To explore the binding mechanisms, I studied the adsorption and desorption processes of the selected organic compounds - propisochlor, 2,4-dichlorophenol. My goal was also to examine the effect of alginite on the decomposition of organic contaminants, which may play a significant role in the implementation of the technology.

Experimental

The sorption tests were carried out in a medium containing phosphate buffer and NaCl at three pH values (pH=5-8), in order to receive information on the influence of pH, the quantity of bound substance (adsorption) and the strength of binding (desorption).

The analysis of contaminants was performed by high performance liquid chromatography (HPLC). The equations were fitted by Freundlich and Langmuir isotherms to the measured isotherm points.

Alginite contains a lot of organic substances, although its composition differs from the humic substances in the soils significantly, since it contains 75 % kerogene which plays a considerable role in binding the organic pollutants. This was supported by the adsorption experiments executed with the alginate cleaned from humic-substances and on bentonite that is a major mineral component. Due to its special composition and chemisorption processes, alginite binds strongly the adsorbed substances in large amounts (> 95%).

The sorption tests indicated that the media with different acidity do not make a considerable difference in the quantities of the binding substances. The desorption tests of alginite provided sorption hysteresis in all of the cases. The reasons can be the decomposition of the examined substances, or that the chemicals adsorbed on the surface, then they diffused into the inner surface of the adsorbent pores, which slowed down the desorption substantially and made it difficult.

It can be deduced from half-lives counted based on the decomposition tests of the chemicals that the decomposition time of the examined substances shortened significantly in the presence of alginite.

New scientific results

Thesis

1. According to my research, 75% of the organic matter of Pula alginite used as an adsorbent consists of a fraction with a uniquely uniform structure, mainly of aliphatic character. The results of NMR studies prove that the purity of Pula alginivegsote is exceptional, and it contains kerogen in a unique form, which has not been reported in the literature.

2. I have proved that experimental conditions and environmental parameters have an effect on the sorption of 2,4-dichlorophenol and propisochlor on alginite.
At the 1:10 adsorbent: solution ratio, the sorption efficiency is above 95% at room temperature, which can be enhanced with increasing temperature. Alginite has a complex buffer system with a strong pH-buffering effect, hence the pH dependence of adsorption is negligible.

3. I have shown experimentally that the amount of natural organic matter in the alginit is the main determining fraction of sorption. The high 2,4-dichlorophenol and propisochlor binding capacity of alginite is determined by the kerogen fraction. The sorption is slightly decreased by the presence of the humic fraction, since the humus behaves as a competing adsorbate in the adsorption on alginite. The presence of clay mineral fraction and carbonates don't influence significantly the sorption, but indirectly they affect the sorption through their strong buffering effect.

4. The binding of hydrophobic propisochlor and 2,4-dichlorophenol can be characterized by the distribution between the specific solid phase of alginite and the aqueous phase. Absorption is also indicated by the fact that the exponent of the Freundlich equation is 1, which formally describes the isotherms, and is characteristic of distribution equilibria.

5. The propisochlor and 2,4-dichlorophenol are capable to be desorbed from the alginite the least, because an irreversible process evolved. The inhibited desorption may be caused by the structure and strong bonds of the active sites of alginite.

6. I assessed that alginite significantly shortens the decomposition time of the propisochlor and the 2,4-dichlorophenol compared to soils. The forming decomposition products, that is, derivates of sulphine- and sulphene-acid could have been identified so far in the literature only in animals, plants and metabolic processes taking place in microorganisms. According to the identified degradation products and the probable degradation pathways, the degradation processes are performed anaerobically and the specific microflora of alginite plays a major role in the degradation processes.

Publications

Related publications to PhD thesis

Publications in international periodicals:

1. Földényi, R., Ertli, T., Lengyel, Zs., **Rauch. R.**:**Retention of Selected Herbicides in Soils, Proceedings of the MTA-OTKA-NSF Project** ,Natural attention of metals along the Tisza river floodplain-wetlands continuum" 2003 (könyv fejezet)

2. **Rauch, R.,** Földényi, R.: **The effect of alginite on the decomposition of the herbicide propisochlor**; Journal of environmental science and health, part B Pesticides, Food Contaminants, and Agricultural Waste 47, 670-676 (2012)

3. **Rauch, R.,** Foldenyi, R. "**Investigation of Organic Matter Content of Hungarian Oil Shale and Its Influence on Sorption of 2,4-Dichlorophenol**", Periodica Polytechnica Chemical Engineering, 64(2), pp. 230-237 (2020)

Publications in Hungarian journals in English:

1. **R. Rauch,** R. Földényi, Zs. Lengyel: **Environmental fate of different herbicides produced in Hungary**; Central European Journal of Occupational and Environmental Medicine (Budapest),6 (2-3), pp. 92-101. (2000)

2. **R. Rauch**, R. Földényi: **Investigation of sorption of 2,4-dichlorophenol on special hungarian oil shale**, Analecta Technica Szegedinensia, Vol 12, No 1, pp. 20-29 (2018)

Conference presentation with full text appearance:

1. **R. Rauch, R.** Földényi, Zs. Lengyel; **Environmental fate of different herbicides produced in Hungary**; regional Conference on Environmental and Health, Szeged, 2000. május 12. (**CEJOEM 2000, Vol.6. No.2-3.:92-101)**

2. **R. Rauch**, R. Földényi: **The effect of organic matter type of hungarian oil shale in sorption of acetochlor**, 25th International Symposium on Analytical and Environmental Problems, 7-8. Oct 2019. (Abstract Book pp. 386-390)

Conference presentation with printed abstracts:

1. **Rauch R**., Földényi, R., Magyar B.,Barcza E.: **The Applicability of alginite in the treatment of contaminated groundwater**; SETAC Europe 12th Annual Meeting; 12-16 May 2002 Vienna, Austria; Challenges in Environmental Risk Assessment and Modelling: Linking Basic and Applied Research,, Abstract Book p.149 (http://abstracts.co.allenpress.com/pweb/setaceu2002/ document/1290)

2. **R. Rauch**, R. Földényi, B. Magyar, I.Barcza: **Study of application of aiginite in the treatment of pesticide contaminated groundwater**; Sixth International Symposium & Exhibition on Environmental Contamination in Central & Eastern Europ and the Commonwealth of Independent States; 1-4 September 2003, Prague, Czech Republic (poster presentation) (Abstract Book 122.pdf)

3. **R. Rauch**, R. Foldenyi, B. Magyar: **Use of special Hungarian oil shale in ground-Water remediation technologies**; 9th FECS Conference and 2nd SFC meeting on chemistry and the Environment 29 August- 1 September 2004, Bordeaux France; (poster presentation) Abstract Book 247. pdf (pp. 344.)

4. Huszka, M., **Rauch, R**., Földényi, R.: **Alginite as a sorbent of organic contaminants**; LACREMED Workshop, 31 Aug-1 Sept 2012, Szeged (Abstract Book pp. 34.)

5. M. Molnár, **R. Rauch**, Ottó Horváth, Rita Földényi: **Investigaton of sorption of potential anthropogenic pollutants on oil shale and its composite forms**, ISAEP 2017, 9-10 Oct 2017, Szeged (Abstract Book pp. 80.))

6. **R. Rauch**, R. Földényi: **Investigation of sorption of 2,4-dichlorophenol on special hungarian oil shale**, International Conference on Science, Technology, Engineering and Economy ICOSTEE 2018 25 October 2018 (poster presentation) (Abstract Book pp. 71.)