

PhD novelty points

**The development and characterization of adsorption and
combined methods for the removal of organic contaminants
from water**

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Recently, the main principle of environmental protection resides in the following sentence: low pollution high energy exploitation. This principle is valid in the use of renewable and geothermal energy, which gains more and more importance. In European context, the thermal water sources of Hungary are significant. As already the name suggests, this thermal water can be used as an energy source while keeping in mind the possible. The temperatures of the thermal waters in Hungary are between 30 °C and 105°C. These waters contain hydrocarbons in relatively small concentrations. This value depends on the water temperature and the localization of the extraction site. Approximately 80 % of the thermal water wells are the source for 80 °C water and are located at Alföld. The emission in the surface waters of the used thermal waters can cause local pollution problems.

The adsorption method is a suitable approach for the removal of organic compounds in low concentrations. The most efficient materials are clay minerals, polyaluminium chlorides or activated carbons. Basically, these adsorbents are the main ones used in modern water treatment technologies. Some of the natural clay minerals can be used as adsorbents. Many organic compounds can interact with the surface of these clay minerals, if they are pre-treated with a cationic surfactant (by the development of an organophilized surface). However, the individual components of an adsorbent system (the nature of the clay mineral, the structure of the organophilic agent, the ionic force and pH of the medium and the chemistry of the pollutants) can affect each other which results various adsorption efficiencies.

The present work targeted the investigation of the removal of organic contaminants (particularly phenolic type compounds) from thermal waters using adsorption methods, advanced oxidation processes and the combination of these two methods.

The organophilized adsorbents are most likely to succeed in the proposed goal, rather than pre-prepared adsorbents. By the adsorption studies, I drew important conclusions concerning the competition for the surface of the adsorbent including the simultaneous pollutant removal. These results can be crucial in case of real applications. Considering that some compounds are difficult to remove by adsorption, it is also necessary to consider the possibility of using a combined removal process (adsorption + highly efficient advanced oxidation process).

To extract more information from the experiments, the adsorption related investigations were carried out both in deionized, model and real thermal water. The removability of the following model compounds were examined in this study: methyl orange, indigo carmine dyes as anionic compounds, thymol, phenol, and sodium-humate were used as usual thermal water components. Four types of bentonites were used as adsorbents (1. Sodium-bentonite SBS - Süd-Chemie AG, CEC = 0.80 mmol / g; 2. Wyoming type sodium-bentonite SPV 200 - AMCOL Specialty, CEC = 0.82 mmol / g; 3. Kunipia-F sodium-bentonite (Kunimine Industries, Japan, JCSS- 3101, CEC = 1.15 mmol / g and 4. Deriton (Unikén Ltd. Hungary CEC = 0.888 mmol / g). The surface of the clay minerals was covered by hexadecyltrimethylammonium-bromide in various ratios (ranging from 40 % - 100 % cationic exchange capacity). This organophilization method was performed in two ways:

- i.) separately pre-organophilized clay mineral
- ii.) organophilization during the treatment (*in-situ* method), when the swollen sodium-bentonite was added to the contaminated water, and after that the required amount of hexadecyltrimethylammonium-bromide (HTAB) was added immediately.

A part of the adsorption studies were also carried out with high basicity polyaluminium chloride (Bopac). Anionic

polyelectrolyte and HTAB were also added to promote the coagulation.

All The adsorption experiments were carried out in a six-paddle "jar test" (Velp JLT6) equipment, in which it is possible to control the mixing time and speed. The advanced oxidation processes were carried out in a recirculation reactor system equipped with ultraviolet / vacuum ultraviolet light source. The production of ozone and the addition of other reagents (like H₂O₂) were also possible in this reactor. The concentration of the model pollutants was determined by a spectrophotometer and by HPLC. The structure of the dried adsorbents and the interaction of HTAB with the clay minerals were examined by X-ray diffraction (XRD) and infrared spectroscopy (FTIR).

During my PhD, I focused on the *in-situ* clay mineral-based adsorbents, which were more efficient than the widely used pre-organophilized adsorbent. Furthermore, it is important to achieve these high removal efficiencies of the in situ method, only a single step is needed. I found that, in case of high CEC values are required. The best example is Kunipia F (1.15 mmol / g) vs. SPV-200 (0.82 mmol / g).

In another series of experiments the surface charge of the clay minerals was modified by four different polyelectrolytes. The results show clearly, that cheap and easy to use clay mineral-based adsorbents are suitable for removing anionic character compounds from water.

It can be stated that the removability of thymol, phenol and sodium-humate as individual pollutants are clearly higher (58-21-98 %) in thermal water than in deionized water. In case of multiple contaminants, the interaction of each compound is also a key factor in the adsorption process. In these experiments the sodium-humate was used which can be found in natural thermal waters.

The degradation of phenol was studied by various high-efficiency oxidation processes, using UV radiation, UV/H₂O₂, ozonization and UV/O₃. It was found that the degradation of pollutants was the most efficient when UV/H₂O₂ was used in deionized water or when ozonization and UV/O₃ was applied in thermal water. Only the half of the energy (100 % energy consumption of the lamp/reactor system is considered when all the phenol is degraded) must be invested to the degradation of phenol to reach the emission limit (90 % decomposition when the starting concentration of phenol was 10 mg / L). The invested energy was 1.55 kJ in the case of using UV/H₂O₂ method and it was 2.65 kJ in the case of using UV/O₃ method in deionized water. In case of thermal water, the invested energy was 3.06 kJ for both of the most efficient methods (O₃ and UV/O₃). It was found that after a partial decomposition by advanced oxidation processes, the remaining phenol can be efficiently removed by adsorption.

New scientific results:

1, I developed a one-step (*in situ*) adsorption method, which has equivalent efficacy to the pre-prepared adsorbent. The great advantage of the new method is that it does not require a separate procedure (with extra work time and cost), previous preparation and storage.

Treatment method	Remained thymol after treatment ($\text{TOC}_T^{\#}$, mg/L) HPLC	Change of total organic carbon (ΔTOC_T , %) HPLC
thymol solution	10	0
M1-Kunipia-F-40	8,6	14,3
M1-Kunipia-F-60	7,7	22,7
M1-Kunipia-F-100	7,5	25,2
M2-Kunipia-F-40	8,7	13,4
M2-Kunipia-F-60	7,6	24,4
M2-Kunipia-F-100	6,4	36,1

[#] TOC_T : total organic carbon of thymol

It was found that the pre-prepared organophilic clay adsorbent (M1) is less efficient than the *in situ* prepared organophilic clays (M2). The removal efficiency can be maximized in each case for the test model compounds (thymol) when 60 to 100 % coverage of the cation exchange capacity is applied. In the case of *in situ* adsorbents

the efficiencies achieved were between 24 % and 36 %, while the pre-prepared adsorbent showed efficiencies between 22 % and 25 %.

2. I found that phenolic compounds can be removed by clay mineral-based adsorbents. The effectiveness of the adsorbent can be influenced when the cation exchange capacity is covered partially or completely by organophilic cation. The differences between the clay minerals can be easily detected, when working in low concentration values (~ 10 mg / L). I found that, in case of any test coverage of the cation exchange capacity, higher percentage of test compounds can be removed from the solution by using the clay mineral with higher cation exchange capacity: (Kunipia-F 1.15 mmol / g), vs. (SPV-200 0,82 mmol/g).

3. I showed that in real/model thermal water matrix humic acid-type of compounds are enhancing the adsorption efficiency of phenolic-type of compounds. In the case of multiple pollutants the adsorption process is influenced multifold. In deionized media, in the presence of sodium-humate, the removal efficiency of phenol (10 %) and thymol (46 %) is higher than in the case when single pollutants are removed. The same time, the removal efficiency of sodium-humate gets somewhat lower (82 %). Examining the adsorption of multiple pollutants in model thermal water, the removal efficiency of phenol was 5 %, thymol 49 % and sodium-humate 100%.

- In deionized water, the functional groups of sodium-humate are accessible, they can connect to the available charged surface sites of the clay mineral. The accessible and less polar chains of sodium-humate will dominate and they will be available for other compounds in the solution with similar polarity (such as phenol type).

- In model/real thermal water, the functional groups of the sodium-humate are surrounded by the ions from solution, therefore a relative charge neutralization occurs on the adsorbent's surface. Hence, sodium-humate can connect to the clay mineral using only its own polar chains – but this happens only at the organophilic surface. Polar or easily polarizable molecules bind to functional groups of sodium-humate which are directed towards water, therefore, no significant differences were observed in the removal efficiency of these molecules. When applying adsorption at industrial scale it is worth considering these interactions.

4. The role of polyelectrolyte is significant in the development of relationships charge of adsorption therefore they have an effect for adsorption of organic molecule on PAC-based adsorbents. The investigated adsorbent consists from high basicity polyaluminium-chloride - Bopac ($c_{PAC} = 80 \text{ mg / L}$) and an anionic polyelectrolyte with high molecular weight ($c_{PE} = 0\text{-}3\text{-}5\text{-}10\text{-}50\text{-}100 \text{ mg/ L}$). Based on the experiments it is concluded, that the removability of both test compounds (thymol, sodium-humate) are increased by increasing the concentration of the polyelectrolyte (in average until the 50 mg / L concentration of polyelectrolyte good removal efficiencies were registered). Above this concentration, the numbers of charges on the surface of the adsorbent decreases together with the presence of the excess polyelectrolyte.

The removability of thymol was 25 % and that of sodium-humate was 28 % (single pollutant) in deionized water. (The adsorbent contained: PAC 80 mg / L and PE 50 mg / L.) Results were better in model thermal water considering both pollutants (thymol 47 % and sodium-humate 95 %).

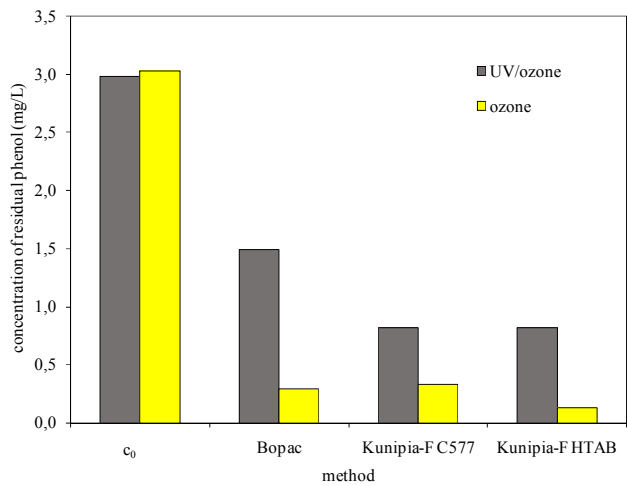
In the presence of multiple pollutants, an inversion is observed in deionized water. In the case of small (0-3-5-10 mg / L)

and too high (100 mg / L) concentration of polyelectrolyte, the removability of the tested compounds was very low (thymol 0-21 %, sodium-humate 7-27 %), but the results were very good (thymol 70 %, sodium-humate 89 % removal) in medium concentration values of the polyelectrolyte 50 mg / L. The lower polyelectrolyte concentration is not enough to overcome the repulsion forces between the particles (PAC and bounded pollutants), because the water does not contain any other ions. By finding the optimal concentration of the polyelectrolyte, the PAC and connected pollutants can form flakes in a short time, so they can be easily removed from the solution.

Above the optimal polyelectrolyte concentration, the formed flakes are too small and they cannot be eliminated by classical gravity driven sedimentation. This was also confirmed by the experiments carried out in model thermal water.

The 50 mg / L polyelectrolyte gives the best result in the studied range, although, the results in the case of thymol are slightly lower than in deionized water. The removal efficiency of the thymol was 55 % and of the sodium-humate was 95 % in model thermal water.

5. Phenolic type of contaminants are effectively removed from the thermal water by advanced oxidation processes (O₃ and UV/O₃) and subsequent adsorption with organophilized clay mineral. The removal of residual contaminants (originating from an advanced oxidation process) and the coagulation-flocculation process under these conditions were investigated. The phenol content of the starting solution (10 mg / L) was decomposed until 70 % by two AOP methods and the remaining phenol was removed efficiently (to ~1 mg / L) by using three different adsorbents.



Scientific activity (MTMT 10014733)

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