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Short communication

Thermal water treatment with granular activated carbon

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Abstract

The object of this article is to discuss the purification of a special thermal water of a geogene origin, containing potentially toxic, organic micropollutants like benzene, toluene, mesitylene, xylene and phenols. As the flotation of the thermal water on model laboratory equipment did not remove all toxic organic substances present from water, a granular activated carbon (GAC) filter column was used. Although the use of granular carbon adsorption is well known in potable water treatment, in industrial water polishing and waste water treatment, there is no information about its use for the purification of special thermal water. The result of the purification with GAC adsorption is thermal water with quality that corresponds to requirements of DIN 19643 for bathing water. After this treatment thermal water reached the hygienic quality of drinking water and could be used for balneological purposes. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Thermal water; Organic micropollutants; Benzene; Toluene; Xylene

1. Introduction

Slovenia is very rich with thermal and mineral water sources. According to the research [1], there are at least 30 natural sources and many more artificial sources of thermal water in Slovenia. There are about 78 sources of thermal water which could produce 129 MW of geothermal energy and have an out-flow of 1353 l/s. The exploitation of about 42 (54%) of locations is 1055 l/s (78%). Most of the above mentioned sources are situated in Pomurje northeast of Slovenia.

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Thermal water is used: (1) as an energy source. If the temperature and the capacity of thermal water are high enough, it is used for geothermal heating (of flats, for industrial purposes, etc.); (2) for balneochemical purposes (physiotherapy in bathing pools and bathtubs): if the temperature of thermal water is at least 40–50°C and water is highly mineralized.

While the temperature and chemical stability are the most important factors for using thermal water as a geothermal source of energy, the compliance with the hygienic demands of the bathing water standards is the most important for its balneological use. The uniqueness of thermal waters in Slovenia is that some waters come from very deep oil exploration wells, where only thermal water was found. These sites are mainly rich with oil and therefore the thermal water is contaminated with organic micropollutants like benzene, toluene, mesitylene, xylene and phenol which in most cases, can be potentially toxic and harmful to human beings. Therefore these waters cannot be accepted as suitable for balneological purposes, unless they are properly treated. All pollutants are of geogene origin and not of anthropogene origin, because industrial contamination is not possible. The physical and chemical characteristics of thermal water differ a lot, although bore-wells do not lie far from each other.

The investigations carried out show that the different balneochemical types of thermal water depend on the mineralization and temperature. The question appears whether it is still allowed to use the organically contaminated water for bathing. The presence of these specific organic substances is not allowed in drinking water and according to the specification, thermal water must be hygienically as pure as drinking water [2]. All organic micropollutants should be reduced below the determined levels.

It could not be found an adequate norm concerning the quality of bathing water contaminated with the specific organic pollutants, so some of the most important health and balneological institutes and experts in Europe and America (Prof. Dr. Raber, personal communication; Dr. Magyarosy, personal communication; Dr. H. Woidich, personal communication; Dr. D. Eichelsdörfer, personal communication) [3] were contacted and asked about the MCL (maximal concentration level) values for these organic substances. It was learned what has been already known: bathing water must have the bacteriological and hygienical quality of drinking water [2]. Opinions about MCL-values differ, so it was decided to reduce all organic micropollutants below their analytical detection limits.

2. Methods and materials

Analyses of cations NH_4^+, Fe^{2+}, Mn^{2+} and anions F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} were determined on a Cary spectrophotometer based on the standard methods (DIN 38406, DIN 38405-D19) [4].

The concentrations of K^+ and Na^+ were measured by an atomic absorption spectrometer (Perkin Elmer 1100 B) using appropriate source of radiation (DIN 38406 E-13, E-14) [5].

Ca^{2+}, Mg^{2+}, HCO_3^-, CO_2 were determined titrimetrically, by standard methods (DIN 38 409 H6) [6].

pH was measured using pH meter (MA 5740), after calibration with buffers of pH 4 and pH 7 (DIN 38404-C5) [7].

The conductivity was measured using conductivity meter (WTW, LF 537) (EN 27888) [8].

Dry residue was measured gravimetrically after evaporating the samples to dryness on a water bath and after drying at 180°C (38409-H1) [9].

Phenols were determined with Gas chromatography–spectrophotometry, while aromatic substances were determined on the basis of DIN 38407-F9-1 [10].

All chemicals used were pro analysis.

3. Purification of thermal water

A lot of experiments were performed to purify the organically contaminated thermal water to make it suitable for bathing. The samples of thermal water for a case study were taken from the well PT-20 in Lendava. Thermal water treatment processes were chosen.

The first attempt was the flotation of organically contaminated thermal water from the well PT-20 on model laboratory equipment. Some results were obtained, but they were far from results which could satisfy the DIN-norm 19643 for bathing water [13]. Only about 20% of all contaminants were removed [11].

The second attempt was the filtration of the thermal water through a sand filter, and then filtrate with organic micropollutants exposed to adsorption on granular activated carbon (GAC) in another filter column.

The height of the sand filter layer was 1.0 m, diameter of the column was 3.2 cm, the velocity of water flow through the sand filter was 10 m/h and the granulometric size of sand grains was 0.5–2 mm, with 63% of 1.0 mm, the contact time was 5 minutes. The organic contaminants should be adsorbed on GAC in the filter column. The height of our GAC layer was 1 m, diameter of the column was 3.2 cm, the velocity of water flow through GAC was 5 m/h and the granulometric size of the GAC grains 1.0 mm, the contact time was 12 minutes. The GAC type was ‘Chemviron F-400’ (information of the activated carbon producer).

4. Results and discussion

Table 1 presents the inorganic substances in thermal water of the source PT-20 before and after the technological treatment. It is very important fact that the inorganic substances remained completely unchanged in water and so the type of the thermal water remained the same as before, i.e. ‘$Na–HCO_3$’. It differs from the ordinary drinking water type, which is in most cases ‘$CaHCO_3$’ or ‘$MgHCO_3$’ and the concentration of Na-ions is much lower. Also the conductivity which indicates the mineralization of the water shows that the sample water has chemically not ordinary drinking water quality, because it is about 6 times higher then average Slovene drinking water conductivity.

Table 1
Inorganic substances in thermal water of the source PT-20 before and after purifying through the sand and GAC filter

	Water from PT-20	Water after purifying
pH (20°C)	7.8	7.8
electroconductivity (mS/cm) (20°C)	2.8	2.8
dry residue (mg/l) (180°C)	1400	1390
cations (mg/l)		
Na^+	350	350
K^+	8.1	8.0
Ca^{2+}	3.8	3.8
Mg^{2+}	15.4	15.4
Fe^{2+}	0.55	< 0.01
Mn^{2+}	0.02	< 0.02
anions (mg/l)		
F^-	2.5	2.5
Cl^-	75	75
Br^-	0.01	0.01
J^-	< 0.01	< 0.01
NO_3^-	4.5	< 0.5
NO_2^-	< 0.01	< 0.01
SO_4^{2-}	< 0.5	< 0.5
HPO_4^{2-}	< 0.1	< 0.1
HCO_3^-	1310	1310

From all inorganic substances only Fe-, Mn- and NO_3-ions have been removed. Fe and Mn were removed already after the sand filtration as insoluble $Fe(OH)_3$ and MnO_2, while NO_3-ions were reduced on GAC.

The aim of the experiments, however, was to remove only the organic pollutants from the thermal water. Table 2 presents the concentrations of organic contaminants before and after our chemical treatment.

Special attention was dedicated to the concentrations of aromatics in thermal water sample, which were relatively high especially benzene 154 $\mu g/l$, toluene 90 $\mu g/l$ and mesitylene 110 $\mu g/l$ while the phenol concentration was only a little bit increased to 2 $\mu g/l$. It is obvious that all these micropollutants were reduced below the present detection limits (< 1 $\mu g/l$).

The temperature of thermal water at the source was 55°C, but the measurements were made at room temperature of 20°C. The question is, what happens with the adsorption of organic substances on GAC at a higher water temperature, considering the fact that the adsorption decreases with the temperature. Therefore, the next experiment was performed at the temperature of about 37°C, like the one in pools. It was proceeded in the same way as described above, except that water was filtered through the sand filter and afterwards on GAC at 37°C, and not at room temperature. The results were practically the same as presented in Table 2. All potentially toxic organic substances (benzene, toluene, xylene, mesitylene, phenol and phenol substances) were reduced below the detection limits (for aromatics below 1 $\mu g/l$, and for phenol derivates below 0.01 $\mu g/l$).

Table 2
The concentration of organic contaminants before and after the treatment of thermal water from PT-20 on GAC filter

Parameters (μg/l)	PT-20	After purifying
2-Metoxyphenol	< 0.01	< 0.01
2-Methylphenol	1.0	< 0.01
Phenol	2.0	< 1
3-Methylphenol + 4-Methylphenol	1.0	< 0.01
2,4-Dimethylphenol	1.4	< 0.01
2-Chlorophenol	< 0.01	< 0.01
2-Nitrophenol	< 0.01	< 0.01
2,4-Dichlorophenol	< 0.01	< 0.01
4-Chloro-3-methylphenol	< 0.01	< 0.01
2,4,6-Trichlorophenol	< 0.01	< 0.01
2,4-Dinitrophenol	< 0.01	< 0.01
2-Methyl-4,6-dinitrophenol	< 0.01	< 0.01
Pentachlorophenol	< 0.01	< 0.01
Benzene	154	< 1
Toluene	90	< 1
Xylene	110	< 1
Mesitylene	50	< 1

The lifetime of GAC can be calculated from the experiments.

If q_e is the mass adsorbed (mg/g), ρ_{GAC} the density of GAC, C_o the influent concentration and C_1 the effluent concentration, then the bed life Y, which is the volume of water that can be treated per unit volume of carbon, can be calculated [12]:

$$Y = q_e \text{ (mg/gGAC)} \cdot \rho_{GAC} \text{ (g/l)}/(C_o - C_1) \text{ (mg/l)} \tag{1}$$

$C_1 = 0$ in case of a strongly adsorbed compound (benzene, xylene, toluene).

The density of GAC F-400 ρ_{GAC} is 425 g/l.

For benzene q_e is 8 mg/g obtained from the isotherm (information of the GAC producer, 1996), $C_o = 1.3$ mg/l The bed life Y for benzene is 21 250 l of water per liter of GAC computed by Eq. (1).

For toluene and xylene q_e are calculated by Freundlich equation:

$$\log q_e = \log K + 1/n \cdot \log C_e \tag{2}$$

where K and $1/n$ are Freundlich's constants, obtained from Table [12] and C_e is the equilibrium concentration.

For toluene, K is 100 and $1/n$ is 0.45, C_e is 0.09 μg/l and according to Eq. (2), q_e is 33.8 mg/g GAC. If $C_o = 0.09$ mg/l, according to Eq. (1) the bed life Y for toluene is 159 792 l of water per liter of GAC.

For xylene, K is 174 and $1/n$ is 0.53, C_e is 0.11 μg/l. According to Eq. (2), q_e is 54 mg/g GAC. If C_o is 0.11 mg/l, then the bed life Y for xylene is 208 681 l of water per liter of GAC according to Eq. (1).

One liter of GAC is therefore sufficient to treat at least 20 000 l of water.

5. Conclusion

We succeeded to purify a thermal water contaminated with traces of phenols, benzene, toluene and mesitylene. The filtration of thermal water first through a sand filter and afterwards through a GAC filter proved to be a satisfactory technological treatment. However, the specifics of thermal waters must be emphasized and each application of granular activated carbon has to be considered individually. A complete laboratory investigation is necessary to determine whether water is directly suitable for balneological purposes or not.

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