# ARCHIVES OF ENVIRONMENTAL PROTECTION

| vol. 36 | no. 4 | pp. 81 - 91 | 2010 |
|---------|-------|-------------|------|
|         |       |             |      |

PL ISSN 0324-8461

© Copyright by Institute of Envionmental Engineering of the Polish Academy of Sciences, Zabrze, Poland 2010

## SORPTION OF IBUPROFEN ON SEDIMENTS FROM THE DOB-CZYCE (SOUTHERN POLAND) DRINKING WATER RESERVOIR

## KATARZYNA STYSZKO<sup>1\*</sup>, KATARZYNA SOSNOWSKA<sup>1</sup>, PIOTR WOJTANOWICZ<sup>2</sup>, JANUSZ GOŁAŚ<sup>1</sup>, JERZY GÓRECKI<sup>1</sup>, MARIUSZ MACHERZYŃSKI<sup>1</sup>

<sup>1</sup> Department of Environmental Sciences in Energy Research, AGH University of Science and Technology, Mickiewicza ave. 30, 30-059 Krakow, Poland

<sup>2</sup> Department of Management and Environmental Protection, AGH University of Science and Technology,

Mickiewicza ave. 30, 30-059 Krakow, Poland

\*Corresponding author e-mail: styszko@agh.edu.pl

Keywords: Sorption, sediments, pharmaceuticals.

**Abstract:** This work determined the solid-water distribution coefficient  $K_d$ , the Freundlich constant  $K_F$  and the organic carbon normalized coefficient  $K_{oc}$  of ibuprofen in natural, aquifer sediments. They are characterized as silt sediments with different clay and sand fraction contents varied in specific surface areas. Content of organic carbon and pH are on the same level. For determining sorption coefficients values of ibuprofen in sediments, its concentration was measured in the aqueous and calculated in the solid phase. Batch tests were conducted following OECD Guideline 106. The resulting  $K_d$  values ranged between 1.14 and 2.29 L/kg,  $K_F$  between 0.25 and 5.48 and  $K_{oc}$  between 1.22 and 2.53 for ibuprofen in sediments S1 and S2, respectively. These experiments proved that the presence of clay minerals beside organic carbon and pH might be relevant in sorption of ibuprofen in sediments. A comparison of experimentally determined  $K_{oc}$  with modelled  $K_{oc}$  calculated on the base of octanol-water partitioning coefficient  $K_{ow}$  shows that the prediction of sorption behaviour cannot be based only on  $K_{ow}$ . This is probably due to the fact that these approaches well describe hydrophobic interactions, but fail to predict sorption of polar and ionic compounds.

## **INTRODUCTION**

Sediments contaminated with organic and inorganic compounds resulting from human activities are recognized as a world-wide problem. Certain amounts of pharmaceuticals and their residues, among other contaminants, enter the aquatic environment and eventually may occur in drinking water. Because of their environmental persistence they may avoid degradation in sewage and drinking-water treatment plants [7, 2, 3]. Ibuprofen is a non-steroidal anti-inflammatory, analgesic and antipyretic drug, used widely. In Germany, diclofenac and ibuprofen, consumed in quantities of ~75 and 180 tons per year respectively [8] have been recognized as important contaminants in the water cycle. They have been found in sewage and surface water samples, for example, in Greece [15], Canada [31], Finland [16], Spain [19], Slovenia [14], United Kingdom [2] and Switzerland [26]. There has been a study of the occurrence of ibuprofen and another 13 pharmaceutical compounds in UK estuarine surface water [28]. In Poland, in 2000 the volume of ibuprofen sold reached 58 t [10].

The introduction of drugs into the environment is a function of the combination of several factors: the quantity manufactured; the dosage (amount frequency and duration); the excretion efficiency of the parent compound and metabolites; the adsorption/ desorption on soil; and the metabolic decomposition in sewage treatment [9]. They are consequently introduced into the surface waters with the effluents and are present in the receiving waters at concentrations in the ng –  $\mu$ g/L range [26, 27, 30]. Ternes *et al.* predicted that two processes are responsible for reduction, namely sorption and biodegradation [27].

At present, there has been continuing research carried out on conditions of the degradation of selected pharmaceuticals in wastewater treatment processes [3, 10, 27, 12, 4, 29, 33]. In long-term investigations of sewage and surface water, studies assessing the possible eco-toxicological effects of detected drug residues are very important, because pharmaceutical compounds found in the aquatic environment usually occur as mixtures, not as single contaminants [26, 6, 21, 17]. Sorption is extremely important because it may dramatically affect the fate and impact of chemicals in the environment. The distribution of a chemical between soil and aqueous phases is a complex process depending on a number of different factors: the chemical nature of the substance, the characteristics of the soil (organic carbon content, clay content, soil texture, pH) and climatic factors (rainfall, temperature, sunlight and wind) [18]. The sorption behaviour of organic contaminants can be reasonably predicted by K<sub>d</sub> values determined in batch experiments. Low K<sub>d</sub> values for ibuprofen reported for primary, and secondary sludge [27, 29] and obtained for digested sludge [5] indicated that in this case, sorption does not play a significant role for the removal of ibuprofen in wastewater treatment plants. According to Urase and Kikuta [29], sorption of acidic pharmaceutical compounds in activated sludge is increased with the decrease in pH. The results of leaching experiments for three types of soils indicated that the leaching potential found could be rated as low for ibuprofen [17]. It means that ibuprofen once applied onto the soil surface, will remain in the upper soil surface and may either be bound by soil particles or may be transformed in the soil [17].

Sorption of polar substances such as pharmaceuticals in different solid matrixes has been of an important concern in the last years and several studies are available in literature dealing with these components in activated sludge [27, 29, 1] and in digested sludge [5]. The solid-water distribution coefficient  $K_{d}$ , the Freundlich constant  $K_{F}$  and the organic carbon normalized coefficient  $K_{oc}$  for ibuprofen, diclofenac and carbamazepine in natural sandy sediments have been reported in Scheytt [22] studies. The sorption of ibuprofen and other pharmaceuticals with relatively high potential ecological risk and high consumption by river sediment samples has been described in Yamamoto *et al.* studies [32].

The aim of this study was to determine the sorption behaviour of ibuprofen to natural, aquifer sediments collected from the Dobczyce drinking water reservoir (Poland). The role of clay fraction in sorption of ibuprofen in sediments has been discussed. Total and organic carbon content, particle size distribution and specific surface area of sediments affecting ibuprofen sorption have been evaluated. The  $K_d$ ,  $K_F$  and  $K_{oc}$  for ibuprofen in natural sediments have been determined. The experimentally determined  $K_{oc}$  values were compared with the modelled  $K_{oc}$  values calculated on the basis of the  $K_{ow}$  (octanol/ water partition coefficient) values. The assessment of sorption of ibuprofen in sediments is of importance for the quality of drinking water in surface reservoir.

### **EXPERIMENTAL**

## Chemicals and materials

Ibuprofen of analytical grade (99% purity) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). It is a weak carboxylic acid with a pK<sub>a</sub> value of 4.52 [20]. Vapour pressure was 2.47 x  $10^{-2}$  [Pa] and solubility 21 mg/L. A stock standard solution of 1000 µg/mL was prepared in methanol. Working standard solutions, at different concentrations, were prepared by appropriate dilution of the stock solution. All solutions were stored at 4°C. Acetonitrile and methanol were HPLC-gradient grade quality from POCH (Gliwice, Poland). Acetone, ethyl acetate (both HPLC grade), potassium dihydrogen phosphate and calcium chloride of analytical grade were obtained from POCH (Gliwice, Poland). In all experiments deionised water (< 0.07 S/cm) from HLP5 pure water system (Hydrolab, Poland) was used. Chromabond EASY polar modified polystyrene-divinylbenzene, (60 mg; 3mL) solid-phase extraction (SPE) cartridges were purchased from Macherey-Nagel (Düren, Germany).

#### Sediments

The sediments were collected in 2005 in the Dobczyce drinking-water reservoir (Southern Poland) which supplies over 50% of the tap water to the city of Krakow and other smaller towns around. It is situated to the south of the city of Krakow on the Raba river at 60 km from the source, 270 m above sea level 125 mln m<sup>3</sup> and has an area covering 970 ha. The main contaminants originate from agriculture and municipal activities with smaller industrial contributions. Samples of sediments were air-dried, sieved through a 2 mm sieve and stored at 4°C. Two types of sediments (S1) and (S2) from inlet and outlet of the reservoir were used in the experiments. Characteristics of the sediments are shown in Table 1.

| Characteristics                                  | Sediment S1 | Sediment S2 |
|--|-------------|-------------|
| Content of particles %                           |             |             |
| (> 2 µm) Clay                                    | 7.3         | 17.8        |
| $(2-63 \ \mu m)$ Silt                            | 81.6        | 79.3        |
| $(63 - 2000 \ \mu m)$ Sand                       | 11.1        | 2.9         |
| Specific surface area m <sup>2</sup> /g          | 12.8        | 31.9        |
| Total carbon g/kg                                | 18.1        | 16.6        |
| Fraction of organic carbon f <sub>oc</sub> kg/kg | 0.015       | 0.016       |
| pH (CaCl <sub>2</sub> )                          | 7.7         | 7.6         |

Table 1. Properties of sediments

Particle size distributions of sediments samples were analysed using a Coulter LS 230 Laser Granulometer (0.04 mm – 2000 mm). Morphology was analysed by Scanning Electron Microscopy (JEOL 5400 (EDS) with a Link ISIS 300 analyser, Oxford Instruments). The microscopic images (Fig. 1) confirmed previously obtained particle size distributions for each sampling point. From the mineralogical point of view the analysed sediments consist mainly of quartz and alumino-silicates [11].

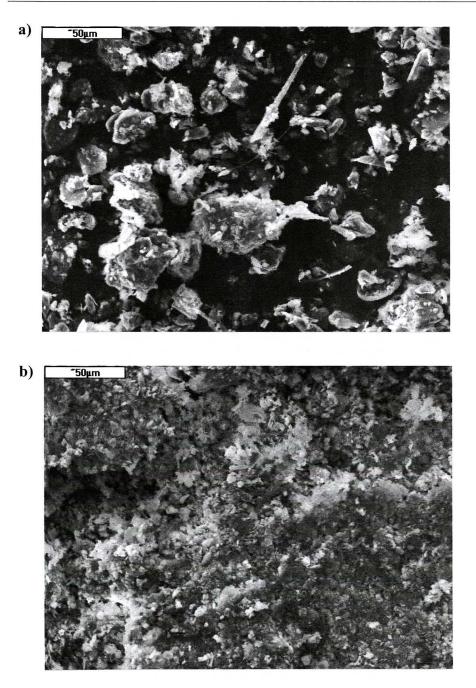


Fig. 1. Scanning electron microscopic images for sediments samples S1(a) and S2(b)

Total carbon and organic carbon were analysed using an ELTRA CS500 instrument. Specific surface areas of sediments were analysed using the BET method (Beckman Coulter SA3100 Analyser). Sediment pH was measured in a solution of 0.01 M CaCl<sub>2</sub>.

#### **Batch** experiments

Batch experiments were conducted as specified by OECD Guideline 106. All experiments were done at room temperature. Ibuprofen sorption for 10  $\mu$ g/L, 20  $\mu$ g/L, 40  $\mu$ g/L, 80  $\mu$ g/L initial concentrations was analysed. Ten grams of sediments were mixed, in dark glass bottles, with 50 mL of 0.01 M CaCl<sub>2</sub> solution, spiked with appropriate working standard solutions and shaken for 24 h using a horizontal shaker at 50 rpm. The sediment suspensions were separated by centrifuging at 2500 rpm for 5 minutes. The aqueous phase was adjusted to pH2 and extracted by solid phase extraction. The concentration of ibuprofen bound to the sediments was measured indirectly as the difference between the concentration at the beginning and the concentration in the solution after equilibration. Control samples with only the test substance in 0.01M CaCl<sub>2</sub> solution (no sediment) were conducted, in the same steps as the test system, in order to check the stability of the test substance and its possible adsorption on the surface of the test vessels. A blank run per sediment with the same amount of sediment and total volume of 50 mL 0.01 M CaCl<sub>2</sub> solution (without test substance) were conducted for both sediment samples.

## Chemical analysis

The analytical procedure for the sediment extracts is shown in Fig. 2.

50 mL sediment extract Adjusted to pH2

SPE (EASY 60mg; 3mL) Elution 3 x 1 mL of ethyl acetate

> Evaporation to dryness Dissolution in 0.1mL of methanol

| HF          | PLC - UV                     | /Vis         |  |  |  |
|-------------|------------------------------|--------------|--|--|--|
| flow rate 1 | mL/min,                      | = 220 nm     |  |  |  |
| Compositio  | on of the n                  | nobile phase |  |  |  |
| Time        | Time Solvent                 |              |  |  |  |
| (min)       | A (%)                        | B (%)        |  |  |  |
| 0           | 40                           | 60           |  |  |  |
| 20          | 55                           | 45           |  |  |  |
| А           | <ul> <li>acetonit</li> </ul> | rile         |  |  |  |
| B –         | 50mM KH                      | $I_2PO_4$    |  |  |  |
|             |                              |              |  |  |  |

Fig. 2. An analytical procedure for sediment extracts analysis

Chromatographic analysis was performed on a Varian HPLC system with pump 9012, UV-Vis detector 9050 and auto-sampler 9100. Separations were carried out using a LiChrospher<sup>®</sup> 100 RP-18 (125 mm x 4 mm i.d. 5  $\mu$ m) cartridge column (Merck, Darmstadt, Germany) protected by a LiChrospher<sup>®</sup> 100 RP-18 (4 mm x 4 mm id. 5  $\mu$ m) guard column (Merck). The limit of detection (LOD) 1  $\mu$ g/L and the limit of quantification (LOQ) 3  $\mu$ g/L was established with the use of standard solutions. Depending on the sample concentration (10 – 80  $\mu$ g/L), the analytical recoveries ranged from 80% to 95% with an R.S.D. between 4.5% to 13%.

#### Sorption coefficients

The distribution coefficient  $K_d$  (Nernst partitioning) is the ratio of the concentration of the substance in the solid phase ( $c_s$ ,  $\mu g/kg$ ) to the concentration of the substance in aqueous solution ( $c_u$ ,  $\mu g/L$ ) at equilibrium.

$$K_{d} = c_{s}/c_{w} \tag{1}$$

Experimentally determined isotherms can commonly be fitted to a relationship of the form:

$$\mathbf{c}_{s} = \mathbf{K}_{F} \, \mathbf{c}_{w}^{1/n} \tag{2}$$

This equation is known as the Freundlich isotherm [23].

The organic carbon normalized sorption coefficient  $K_{oc}$  related to the sorption coefficient to the organic carbon content (fraction of organic carbon  $f_{oc}$ ) of the sample:

$$K_{\rm OC} = K_{\rm F} / f_{\rm OC}$$
(3)

#### **RESULTS AND DISCUSSION**

Sediment S1 coming from the initial settling trap for suspension, in the first part of reservoir is coarse material with higher content of sand fraction. In the deeper part of reservoir, close to the dum, is fine material, mainly consisting of clay and silt. The content of organic carbon and pH in both tested sediments are the same, so better sorption of ibuprofen on sediment S2 might be caused by higher amount of clay minerals in this sediment and conjugate with its higher specific surface area.

Sorption coefficients for sediment S2 are significantly higher than those obtained for sediment S1 (Tab. 2).

| Sample | K <sub>d</sub><br>L /kg | $K_{F}$ $\mu g^{1-1/n} L^{1/n}/kg$ | logK <sub>oc</sub> | 1/n  | r <sup>2</sup> | N  |
|--------|-------------------------|------------------------------------|--------------------|------|----------------|----|
| S1     | 1.14                    | 0.25                               | 1.22               | 1.44 | 0.90           | 8  |
| S2     | 2.29                    | 5.48                               | 2.53               | 0.78 | 0.89           | 12 |

Table 2. Distribution coefficients K<sub>d</sub>, K<sub>oc</sub> and K<sub>F</sub> of ibuprofen in sediments

N - number of samples

In the case of sediment S1 sorption of ibuprofen should be considered mainly on organic matter. In the case of sediment S2 besides sorption on organic carbon, reaction of carboxylic group of ibuprofen with metals (Fe, Al) contained on the surface of the solid (clay minerals) should be considered. In this case a hydroxyl bound to a metal in the solid is displaced by the organic sorbate. Distribution coefficients  $K_{a}$  and organic carbon normalised sorption coefficient K<sub>oc</sub> for each tested sediment were on the similar level. However, most sorption coefficients values were of the same order of magnitude, but remarkably lower for sediment S1. Ibuprofen sorption coefficients determined for natural sandy sediments determined by Scheytt [22] K<sub>d</sub> varied from 0.18 to 1.69 L/kg, K<sub>F</sub> from 0.21 to 0.83 and  $K_{oc}$  from 2.14 to 2.21 for direct and indirect method, respectively. Sediment used by Scheytt [22] in batch experiment was characterized by higher sorption of ibuprofen although lower content of organic carbon ( $f_{oc}$  0.002–0.0013) in comparison to sediments used in our experiment, which might indicate that other sediment properties rather than organic carbon are crucial for sorption of ibuprofen. In this case pH might play main role in sorption of ibuprofen. The sediment used in batch experiment by Scheytt [22] was characterized by lower pH (4.8–6.7) than sediments tested in the current study. In those tested sediments with a pH of 4.8, the carboxyl group of ibuprofen should be at least partly protonated leading to a better sorption onto organic matter because of distinct lipophilicity in its indissociated form. The higher sorption coefficients for sediments with a higher organic carbon content ( $f_{oc}$  0.00075, 0.0087, 0.017) were obtained in Yamamoto study [32].

The sorption data were fitted to the logarithmic transform of the Freundlich equation (Fig. 3).

 $\rm K_F$  values were found to be 0.25 and 5.48 for sediment S1 and S2, respectively. According to Schwarzenbach a value of n < 1 in the Freundlich equation reflects the situation in which at higher sorbate concentrations, it becomes more and more difficult to sorb additional molecules. Specific binding sites become filled or remaining sites are less attractive to the sorbate molecules [11]. The n > 1 in this case describes a situation in which previously sorbed molecules lead to the modification of the surface which favours further sorption. The n values determined from 1/n in the Freundlich equations for sediment S1 is 0.7 and 1.3 for sediment S2. There were significant differences between the  $\rm K_d$  values and the Freundlich constants, mostly due to the non-linearity of the isotherm. Organic carbon normalised sorption coefficients  $\rm K_{oc}$  have been calculated and shown to be very helpful in reducing the variability of results.

 $K_{oc}$  values are often estimated based on the  $K_{ow}$  (octanol/water partition coefficient) values. Comparison of  $K_{oc}$  calculated on the basis of correlation equations of Karickhoff<sup>1</sup> (log  $K_{ow} = 3.5$  [31], log  $K_{oc} = 3.29$ ) [13] and Sontheimer<sup>2</sup> (log  $K_{ow} = 3.5$  [31], log  $K_{oc} = 2,89$ ) [24] and Scheytt<sup>3</sup> (log  $K_{ow} = 2.48$ , log  $K_{oc} = 2,27$ ) [21] with experimental data showed that calculated values did not match the experimental data with the exception of the Scheytt [21] value, but only for sediment S2. The reason may be that ibuprofen is a carboxylic acid. There are negatively charged ions present, so ionic character plays a major role for sorption of ibuprofen at the tested pH (7.6; 7.7). The presence of polar functional group which might interact only with special parts of organic matter and minerals

<sup>1 [26]</sup>  $(\log K_{oc} = 1.01 \log K_{ow} - 0.21)$ 

<sup>2 [28]</sup>  $(\log K_{oc} = 0.807 \log K_{ow} + 0.068)$ 

<sup>3</sup> Value based on equation by Karickhoff

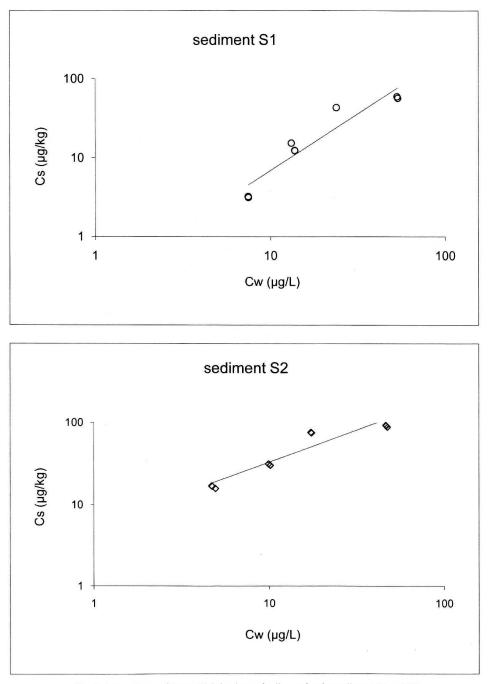


Fig. 3. Linear form of Freundlich isotherm for ibuprofen for sediment S1 and S2

## CONCLUSION

A comparison sorption coefficients of ibuprofen reported in the literature for natural sandy sediments with values of sorption coefficients obtained in presented experiments showed that pH should be considered as one of crucial properties of sediments. Furthermore, the presence of clay minerals might play a significant role in sorption of ibuprofen in sediments. In both sediments tested with pH above 7.5, the carboxyl group of ibuprofen occurs in its charged forms so ionic character plays a major role for sorption. The results as those reported in the literature show that the prediction of sorption behaviour cannot be based only on  $K_{ow}$ . This is probably due to the fact that these approaches well describe hydrophobic interactions, but fail to predict sorption of polar and ionic compounds.

#### Acknowledgement

This work was supported by the AGH University grant no 11.11.210.199 and by the Kościuszko Foundation, American Center for the Polish Culture with the funds provided by Alfred Jurzykowski Foundation.

### REFERENCES

- Andersen H.R., M. Hansen, J. Kjolholt, F. Stuer-Lauridsen, T. Ternes, B. Halling-Sorensen: Assessment of the importance of sorption for steroid estrogens removal during activated sludge treatment, Chemosphere, 61, 139-146 (2005).
- [2] Ashton D., M. Hamilton, K.V. Thomas: Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom, Sci. Total Environ., 333, 167-184 (2004).
- [3] Beausse J.: Selected drugs in solid matrices: a review of environmental determination, occurrence and properties of principal substances, TrAC, Trends Anal. Chem., 23, 753-761 (2004).
- [4] Carballa M., F. Omil, J.M. Lema, M. Llompart, C. Garcia-Jares, I. Rodriguez, M. Gomez, T. Ternes: Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant, Water Res., 38, 2918-2926 (2004).
- [5] Carballa M., G. Fink, F. Omil, J.M. Lema, T. Ternes: Determination of the solid-water distribution coefficient (Kd) for pharmaceuticals, estrogens and musk fragrances in digested sludge, Water Res., 42, 287-295 (2008).
- [6] Cleuvers M.: Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen, and acetylsalicylic acid, Ecotox. Environ. Safe., 59, 309-315 (2004).
- [7] Daughton Ch.C., T.A. Ternes: Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change?, Environ. Health Persp., 107 (Supplement 6) (1999).
- [8] Daughton Ch.C. and T. Jones-Lepp, eds. *Pharmaceuticals and Personal Care Products in the Environment*, Scientific and Regulatory Issues, American Chemical Society Symposium Series 791, Washington, DC.: ACS/Oxford University Press (2001).
- [9] Diaz-Cruz M.S., M.J. Lopez de Alda, D. Barcelo: Environmental behavior and analysis of veterinary and human drugs in soils, sediments and sludge, TrAC, Trends Anal. Chem., 22, 340-351 (2003).
- [10] Felis E., K. Miksch, J. Surmacz-Górska, T. Ternes: Presence of pharmaceutics in wastewater from waste water treatment plant "Zabrze - Śródmieście" in Poland, Arch. Environ. Prot., 31, 49 (2005).
- [11] Golas J., B. Kubica, W. Reczynski, W.M. Kwiatek, M. Jakubowska, M. Skiba, M. Stobiński, E.M. Dutkiewicz, G. Posmyk, K.W. Jones, M. Olko, J. Gorecki: *Preliminary studies of sediments from the Dobczyce drinking water reservoir*, Pol. J. Environ. Stud., 14, 577-584 (2005).
- [12] Joss A., S. Żabczyński, A. Goebla, B. Hoffmann, D. Loffler, Ch. S. McArdell, T.A. Ternes, A. Thomsen, H. Siegrist: *Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme*, Water Res., 40, 1686-1696 (2006).

#### 90 K. STYSZKO, K. SOSNOWSKA, P. WOJTANOWICZ, J. GOŁAŚ, J. GÓRECKI, M. MACHERZYŃSKI

- [13] Karickhoff S.W., D.S. Brown, T.A. Scott: Sorption of hydrophobic pollutants on natural sediments, Water Res., 13, 241-248 (1979).
- [14] Kosjek T., E. Heath, A. Krbavcic: Determination of non-steroidal anti-inflammatory drug (NSAIDs) residues in water samples, Environ. Int., 31, 679-685 (2005).
- [15] Koutsouba V., T. Heberer, B. Fuhrmann, K. Schmidt-Baumler, D. Tsipi, A. Hiski: Determination of polar pharmaceuticals in sewage water of Greece by gas chromatography-mass spectrometry, Chemosphere, 51, 69-75 (2003).
- [16] Lindqvista N., T. Tuhkanenb, L. Kronberg: Occurrence of acidic pharmaceuticals in raw and treated sewages and in receiving waters, Water Res., **39**, 2219-2228 (2005).
- [17] Oppel J., G. Broll, D. Loffler, M. Meller, J. Rombke, T. Ternes: Leaching behaviour of pharmaceuticals in soil-testing-systems: a part of an environmental risk assessment for groundwater protection, Sci. Total Environ., 328, 265-273 (2004).
- [18] Organization for Economic Cooperation and Development, OECD Guideline for the testing of chemicals - 106, Adsorption – Desorption Using a Batch Equilibrium Method (2000).
- [19] Rodriguez I., J.B. Quintana, J. Carpinteiro, A.M. Carro, R.A. Lorenzo, R. Cela: Determination of acidic drugs in sewage water by gas chromatography-mass spectrometry as tert.-butyldimethylsilyl derivatives, J. Chromatogr. A, 985, 265-274 (2003).
- [20] Roses C.R.M., E. Bosch: A comparison between different approaches to estimate the aqueous pKa values of several non-steroidal anti-inflammatory drugs, Anal. Chim. Acta, 338, 127-134 (1997).
- [21] Scheytt T., P. Mersmann, R. Lindstadt, T. Heberer: 1-Octanol/Water Partition Coefficients of 5 Pharmaceuticals from Human Medical Care: Carbamazepine, Clofibric Acid, Diclofenac, Ibuprofen, and Propyphenazone, Water Air Soil Poll., 165, 3-11 (2005).
- [22] Scheytt T., P. Mersmann, R. Lindstädt, T. Heberer: Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments, Chemosphere, 60, 245-253 (2005).
- [23] Schwarzenbach R.P., P.M. Gschwend, D.M. Imboden: *Environmental Organic Chemistry*, Jonh Wiley and Sons, Inc., New York 1993.
- [24] Sontheimer H., P. Cornel, M. Seym: Untersuchungen zur Sorption von aliphatischen Chlorkohlenwasserstoffen durch Böden aus Grundwasserleitern, Veröffentlichungen des Bereichs und des Lehrstuhls für Wasserchemie der Universität Karlsruhe, Heft, 22 (1983).
- [25] Stuer-Lauridsen F., M. Birkved, L.P. Hansen, H.C. Holten Lützhøft, B. Halling-Sørensen: Environmental risk assessment of human pharmaceuticals in Denmark after normal therapeutic use, Chemosphere, 40, 783-793 (2000).
- [26] Tauxe-Wuersch A., L.F. De Alencastro, D. Grandjean, J. Tarradellas: Occurrence of several acidic drugs in sewage treatment plants in Switzerland and risk assessment, Water Res., 39, 1761-1772 (2005).
- [27] Ternes T.A., N. Herrmann, M. Bonerz, T. Knacker, H. Siegrist: A rapid method to measure the solid-water distribution coefficient (Kd) for pharmaceuticals and musk fragrances in sewage sludge, Water Res., 38, 4075-4084 (2004).
- [28] Thomas K.V., M.J. Hilton: The occurrence of selected human pharmaceutical compounds in UK estuaries, Mar. Pollut. Bull., 49, 436-444 (2004).
- [29] Urase T., T. Kikuta: Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process, Water Res., 39, 1289-1300 (2005).
- [30] Wezel van A. P., T. Jager: Comparison of two screening level risk assessment approaches for six disinfectants and pharmaceuticals, Chemosphere, 47, 1113-1128 (2002).
- [31] Xiu-Sheng Miao, B.G. Koenig, C.D. Metcalfe: Analysis of acidic drugs in the effluents of sewage treatment plants using liquid chromatography–electrospray ionization tandem mass spectrometry, J. Chromatogr. A., 952, 139-147 (2002).
- [32] Yamamoto H., Y. Nakamura, S. Moriguchi, Y. Nakamura, Y. Honda, I. Tamura, Y. Hirata, A. Hayashi, J. Sekizawa: Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: Laboratory photolysis, biodegradation, and sorption experiments, Water Res., 43, 351-362 (2009).
- [33] Yu J.T., E.J. Bouwer, M. Coelhan: Occurrence and biodegradability studies of selected pharmaceuticals and personal care products in sewage effluent, Agr. Water Manage., 86, 72-80 (2006).

Received: March 11, 2010; accepted: July 15, 2010.

#### SORPCJA IBUPROFENU NA SEDYMENTACH POCHODZĄCYCH ZE ZBIORNIKA WODY PITNEJ W DOBCZYCACH

W niniejszej pracy oszacowano stopień sorpcji ibuprofenu na sedymentach pobranych ze zbiornika wody pitnej w Dobczycach poprzez wyznaczenie współczynników podziału K<sub>d</sub>, ciało stałe-roztwór wodny, stałych Freundlicha K<sub>F</sub> oraz współczynników adsorpcji znormalizowanych względem węgla organicznego K<sub>OC</sub>. Proces sorpcji ibuprofenu badano na dwóch sedymentach (S1, S2) o zbliżonej zawartości węgla organicznego oraz pH, zróżnicowanych natomiast pod względem składu granulometrycznego i wielkości powierzchni właściwej. Analizy wykonano opierając się na wytycznych normy OECD nr 106. Eksperymentalne wartości współczynników charakteryzujących sorpcję ibuprofenu dla sedymentów S1 i S2 wynoszą odpowiednio: K<sub>d</sub> ~ 1.14 i 2.29 L/kg, K<sub>F</sub> ~ 0.25 i 5.48 oraz K<sub>OC</sub> ~ 1.22 i 2.53. Wykazano, iż zawartość frakcji gliniastej obok zawartości współczynnika modelową wartość współczynnika K<sub>OC</sub> obliczoną na podstawie współczynnika modelową wartości eksperymentalną K<sub>OC</sub>. Wykazano, iż zdolności sorpcyjne związków nie mogą być prognozowane tylko w oparciu o wartość K<sub>OW</sub>, gdyż współczynnik ten nie opisuje sorpcji związków polarnych i jonowych.