

Thermodynamic and Kinetic Aspects of Mercury Sorption on Activated Carbon in the Process of Mercury Bioreduction

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A unique biotechnological method for remediation of industrial wastewater contaminated by toxic mercury, based on the enzymatic reduction of ionic mercury by live bacteria, has been developed by prof. Deckwer and co-workers at GBF (at present HZI), Germany, and implemented in a pilot-plant scale. The experience gained during operation of this installation led to the idea, that the process of bioremediation may be integrated in one bioreactor with the adsorption of mercury by immobilization of the bacteria onto the activated carbon. For this it was necessary to define several significant parameters of the activated carbon selected for the process and the adsorption process itself.

The paper presents results of the equilibrium and kinetics investigations of the process of ionic mercury sorption from aqueous solutions onto 8 different types of activated carbon. The effective diffusion coefficients in the carbon particles were obtained from the transient-state experiments using a mathematical model of the process and the sorption isotherms as well as the saturation capacity of the sorbents in relation to ionic and metallic mercury were identified. From the temperature dependence of adsorption constants the values of adsorption enthalpy for both metallic and ionic mercury on activated carbon impregnated with sulfur were estimated. The obtained results enabled selection of the optimal sorbent for the fixed-bed activated-carbon bioreactor which will be applied for the modified, integrated process of biological detoxification of mercury in industrial wastewaters.

Key words:

Adsorption, mercury bioreduction, wastewater bioremediation, activated carbon, bio-process integration

Introduction

Mercury is a naturally occurring substance with unique chemical and physical properties but with no known essential biological function either for humans or for other organisms. All forms of mercury are toxic for humans and virtually to all other forms of life, but the most dangerous are soluble inorganic salts of mercury and its organic compounds, like methylmercury. Mercury in any form can cause serious health and ecological problems when released to the environment in high concentration resulted by human activities, because in specific conditions it may be biologically transformed from low-soluble metallic mercury, or even non-soluble HgS, to soluble and extremely toxic methylmercury. Mercury is responsible for the most serious outbreaks of metal poisoning, e.g. so-called Minamata tragedy.¹

Nowadays, the major anthropogenic sources of mercury include burning of coal to produce electricity, incineration of waste and the chloro-alkali

industry. The so-called chloro-alkali industry produces chlorine and alkali, sodium hydroxide or potassium hydroxide, by electrolysis of the NaCl (or KCl) salt solution. There are three different techniques based on the brine electrolysis but the mercury pollution is specific only for the mercury cell technology, which was invented and is still the most common method used for chlorine production in Europe. Due to characteristics of this process, mercury can be emitted through air, wastewater, solid wastes as well as in the products. Total mercury emission only from chlor-alkali plants in Europe was estimated for about 35 tones in 2006, ranging from 0.1 – 3.0 g of Hg per 1 ton of chlorine capacity at different plants.^{2,3}

Hence, it must be stated that mercury is a priority, global pollutant because of its extreme toxicity, global atmospheric transport – resulting from high Hg volatility, and accumulation in the food chain. Removal of mercury from industrial emissions is therefore mandatory and should take into account the latest achievements in science and technology.

A number of technologies have been developed over the years to remove toxic metal ions from water. Such methods include chemical precipitation, electrodeposition, ultra filtration, ion-exchange, adsorption and biological processes. Adsorption, compared to other methods, appears to be a simple and attractive process in view of its high efficiency, easy handling and cost-effectiveness as well as the availability of wide range of different adsorbents. In addition, especially in the case of metallic mercury, the possibility of pure metal recovery for recycle and reuse of the regenerated adsorbent is the further advantage. The search for an effective, low-cost and environmentally friendly sorption materials resulted in the increasing interest in different sorbents of biological origin, like microalgae,^{4,5} live or inactivated bacterial cells,^{6–8} fungi,^{9,10} biopolymers^{9,11} or even vegetation waste materials.¹²

A unique biotechnological method for the remediation of industrial wastewater contaminated by toxic mercury, based on the enzymatic reduction of ionic mercury by live mercury-resistant bacteria has been developed by prof. Deckwer and co-workers at GBF (at present Helmholtz Zentrum fuer Infektionsforschung, HZI), Braunschweig, Germany, and implemented in the pilot-plant scale.^{13–17} The so-called *bioMER* installation essentially consisted of a 1 m³ bioreactor filled with porous pumice stones as a carrier material for immobilization of microorganisms and an activated carbon filter of 0.7 m³ volume as a polishing step. (Fig. 1)

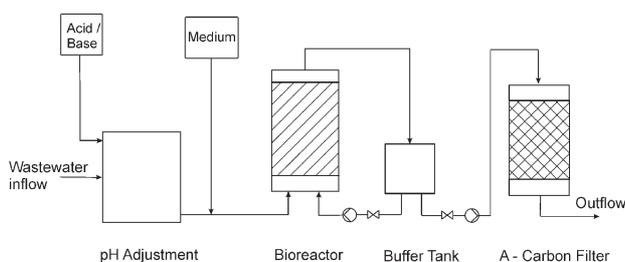


Fig. 1 – Flow scheme of the *bioMER* plant for continuous treatment of chloralkali electrolysis factory effluent^{14,15}

The microorganisms used in the original *bioMER* installation were natural (i.e. not engineered genetically), non-pathogenic soil bacteria (a mixture of seven subspecies of *Pseudomonas putida*, *stutzeri* and *fulva*), isolated from river sediments of the Spittelwasser river, a tributary of the Elbe river (Germany), which possessed natural mercury resistance.^{16,18} These strains are able to convert enzymatically reactive ionic mercury to elemental mercury, which remains in the packed bed of the bioreactor as water-insoluble metal and is no longer toxic for the bacteria. To enable the

bio-transformation the micro organisms must be fed with a nutrient medium (e.g. containing sucrose and yeast extract) and require aerobic conditions, whereby the usual oxygen saturation of wastewater (6–8 mg O₂/L) is sufficient. An activated carbon filter was used in the *bioMER* installation as a polishing filter to reach a final concentration of mercury less than 50 µg/L (the EU Hg discharge limit for wastewaters from chlor-alkali industry,^{19,20} but more than 90 % of the mercury removal was obtained in the bioreactor, as an effect of microbial activity.

The experience gained during operation of the pilot-plant installation led to the idea, that the process of bioremediation may be integrated in one piece of apparatus with the adsorption of ionic mercury from wastewater and metallic mercury formed during the process, by immobilization of the bacteria directly on the activated carbon used as a packing in a fixed-bed bioreactor. In order to apply such solution in practice it was necessary to select the optimal adsorbent and to define several significant equilibrium and kinetic parameters of the process of ionic and metallic mercury adsorption onto selected activated carbon.

Hence, the aim of the presented investigations was to identify the equilibrium and kinetics parameters of the process of ionic and metallic mercury sorption from aqueous solutions onto several types of activated carbon. The sorption isotherms, saturation capacity of the sorbents and its dependence on the temperature were identified and then the effective diffusion coefficients in the carbon particles were obtained from the transient-state experiments using a mathematical model of the process. This work should be considered as the first, but important step leading to the application of the new technology in industrial scale.

Experimental

The batch ionic mercury adsorption experiments were carried out by shaking 0.5 g of activated carbon together with 100 ml aqueous solution of HgCl₂ of the desired concentration (in 300 ml glass flasks) at various retention times (ranging from 10 minutes to 6 days) in a temperature-controlled shaker (B. Braun BS-1, Germany). In the preliminary experiments it was found that the period of 1–5 days (depending on the temperature) was sufficient for the obtaining of the Hg sorption equilibrium. The results of measurements of Hg concentration changes in the course of the sorption process were applied for the identification of the diffusion coefficients of mercury ions in the activated carbon particles, using the mathematical

model of the process, described below. The pH of the solutions were adjusted to constant value of 7 by means of ultrapure HCl (Baker chemicals for Hg analysis). Continuous mixing was assured during the experiments by a constant rotational speed of the shaker of 110 rpm. The flasks were withdrawn from the shaker at suitable time intervals and the samples of a liquid were taken (only one sample from each flask), filtered through a 0.45 μm microporous membrane filter (to separate carbon particles) and then analyzed for mercury contents by the cold vapor technique using the RA-915+ (Lumex, Russia) mercury analyzer. It was checked that filtration did not have influence on ionic mercury concentration in the solution.

In order to investigate in a similar way adsorption equilibrium of metallic form of mercury it was necessary to obtain mercury solutions of much higher concentration than Hg^0 solubility in water at room temperature (i.e. about 50 $\mu\text{g/L}$). Such solutions, or it is better to say: micro-suspensions, of metallic mercury concentrations 800 – 1000 $\mu\text{g/L}$, were obtained by means of an ultrasound bath and then checked for their stability under the same conditions as the equilibrium experiment. It was found that the increased mercury concentration was stable over the period of 5 – 6 days which was enough for the adsorption isotherms investigations; during this time mercury did not sediment down and its concentration did not change significantly. It was assumed that Hg^0 sorption conditions onto activated carbon in the above mentioned solution/micro-suspension of increased mercury content are similar to those in a fixed-bed bioreactor, where Hg^0 is a product of the bioreduction reaction, being released to a liquid phase by cells at a high rate. To avoid metallic mercury evaporation and oxidation during equilibrium experiments the flasks were tightly corked and before closing flasks the air over the liq-

uid surface was replaced with pure nitrogen under the atmospheric pressure.

Sorbents used in experiments

All types of activated carbon used in the experiments were commercial carbons prepared for industry and available in the market; it is important for the modified bioremediation technology from the economic point of view. Applied activated carbons differ from each other in preparing technique, porosity, amount of sulfur content and mean diameter of a particle.

Mean diameter of a sorbent granule and number of its granules in 1 g of activated carbon was calculated experimentally, using optical analysis system *Olympus Micro Image* (v. 5.0). The most important properties of investigated sorbents were placed in the table 1.

Adsorption model

Equilibrium adsorption data were fitted with the Langmuir equation

$$q = \frac{q_m \cdot b \cdot c_{\text{eq}}}{1 + b \cdot c_{\text{eq}}} \quad (1)$$

where:

- b – Langmuir constant, L mg^{-1} ,
- c_{eq} – equilibrium concentration of Hg(II) , mg L^{-1} ,
- q – amount of the Hg(II) adsorbed per unit mass of the adsorbent, mg g^{-1} ,
- q_m – saturation sorption capacity of the sorbent, mg g^{-1} ,

The Langmuir equation parameters, q_m and b , may be easily established by linear regression of the the linearized form of the above equation:

Table 1 – Basic properties of the active carbons used in experiments

Lp	Type of activated carbon	Producer	Amount of sulfur, % wt	Bulk density, kg m^{-3}	d_{mean} , mm	Raw material
1.	102183	Merck	not impregnated	~300	0.08	Wood carbon
2.	POOL 1-3	CarboTech	not impregnated	400 \pm 50	2.39	Wood carbon
3.	POOL 1-3+S	CarboTech	~5 %	400 \pm 50	2.41	Wood carbon
4.	POOL 0,5-1,6	CarboTech	not impregnated	510 \pm 30	0.91	Wood carbon
5.	DG 1-3+S	CarboTech	~5 %	460 \pm 50	2.21	Hard coal
6.	DGC 0,1- 0,5	CarboTech	not impregnated	~300	0.38	Coconut shell carbon
7.	NORIT RBHG 3	Norit	<10 %	200-600	4.31	Pressed wood carbon

$$c_{\text{eq}} = q_m \cdot \frac{c_{\text{eq}}}{q} - \frac{1}{b}, \quad (2)$$

where the reciprocal of the Langmuir constant, $1/b$, may be considered as a sorption process equilibrium constant, $K[\text{mg L}^{-1}]$.

Diffusion coefficients inside pores of a sorbent granule were obtained using an intra-particle diffusion model. The model equations were formed on the basis of the process scheme, shown in Fig. 2.

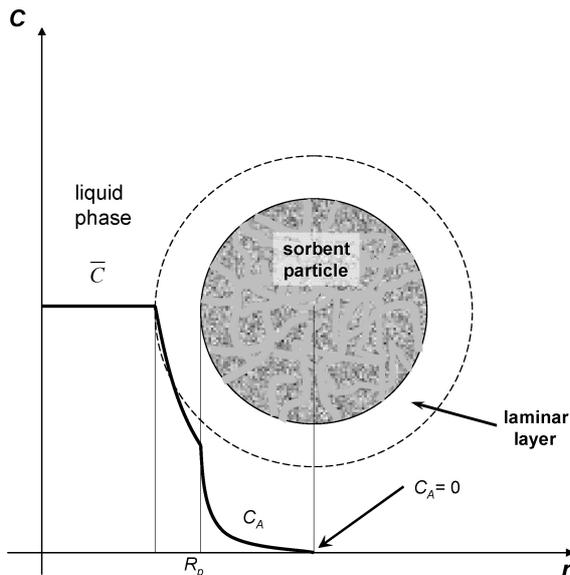


Fig. 2 – Profile of Hg^{2+} concentration around and inside of a sorbent particle

The mass balance of mercury ions in the liquid phase around the sorbent particle may be expressed by the equation:

$$-V \frac{d\bar{c}}{dt} = \int_{A_p} k_f (c_0 - c_A|_{r=R_p}) dA \quad (3)$$

and inside a spheric particle by the following relation:

$$\frac{\partial c_A}{\partial t} + \left(\frac{1 - \varepsilon_p}{\varepsilon_p} \right) \rho_s \frac{\partial q_A}{\partial t} = D_{\text{Ap}} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_A}{\partial r} \right) \quad (4)$$

where:

- V – volume of the solution, m^3
- A – external surface area of the sorbent particle, m^2
- t – time, s
- D_{Ap} – intra-particle diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
- k_f – film mass transfer coefficient in a liquid phase, m s^{-1}
- ε_p – particle porosity, –
- ρ_s – solid particle density, kg m^3

Assuming that the adsorption rate is much higher than diffusion rate and introducing the Langmuir isotherm equation, the following relation may be obtained:

$$\frac{\partial q_A}{\partial t} = \frac{\partial q_A}{\partial c_A} \frac{\partial c_A}{\partial t} = \frac{b_A q_{\text{Am}}}{(1 + b_A c_A)^2} \frac{\partial c_A}{\partial t}, \quad (5)$$

which introduced into the basic model equation (4) gives finally the relation:

$$\left[1 + \left(\frac{1 - \varepsilon_p}{\varepsilon_p} \right) \frac{b_A q_{\text{Am}} \rho_s}{(1 + b_A c_A)^2} \right] \frac{\partial c_A}{\partial t} = D_{\text{Ap}} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_A}{\partial r} \right) \quad (6)$$

The following boundary and initial conditions were assumed:

($t \geq 0$):

$$\left. \frac{\partial c_A}{\partial r} \right|_{r=0} = 0 \quad (7)$$

$$-\varepsilon_p D_{\text{Ap}} \left. \frac{\partial c_A}{\partial r} \right|_{r=R_p} = k_f (c_{A0} - c_A|_{r=R_p}), \quad (8)$$

($t = 0$):

$$c_A = 0 \quad \text{for} \quad 0 \leq r \leq R_p \quad (9)$$

The model calculations for the consecutive periods of time during the mercury sorption on activated carbon allow to predict mercury concentration changes in the liquid phase inside pores of a sorbent particle (example of such simulation for the values of model parameters obtained from the experimental results is presented in Fig. 3a, 3b, 3c). The presented graphs were obtained using graphic program FemGV, v. 6.3 (FEMSys Ltd., United Kingdom). Mercury concentration in the liquid phase showed in the graph legend is expressed in g L^{-1} .

The above model was used to identify diffusion coefficients in a sorbent particle on the basis of transient-state experimental data, i.e. changes of mercury concentration in the liquid phase during the batch sorption process. Assuming ideal mixing in the liquid phase, the resistance for mass transfer in a liquid film surrounding the particle may be neglected. During the experiments it was verified that rotational speed of the shaker had no influence on the equilibrium time of the adsorption process (i.e. adsorption rate), which proves that the assumption of very good mixing conditions is justified for the applied range of a shaker rotational speed. It was also assumed that the diffusion coefficient is independent on the mercury concentration and that all

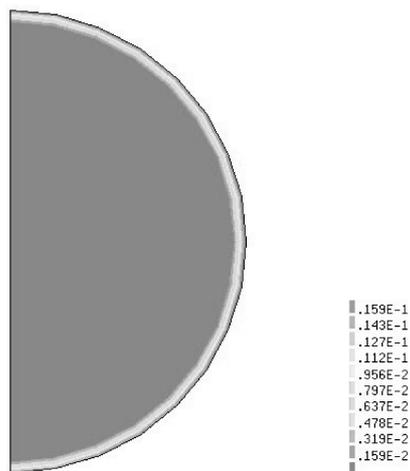


Fig. 3 a – Calculated mercury concentration profile in the liquid phase inside the activated carbon particle after 45 minutes of the Hg^{2+} sorption process (activated carbon type DG(1-3)+S, $C_0 = 0.330 \text{ g L}^{-1}$, temp. $25 \text{ }^\circ\text{C}$)

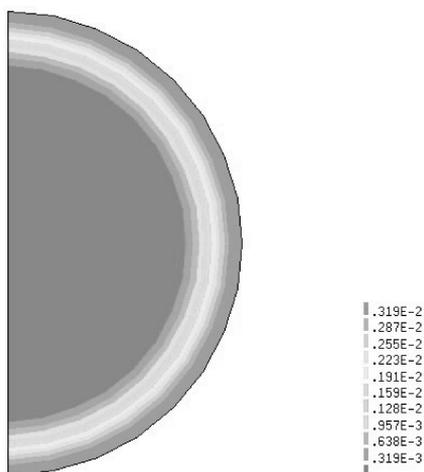


Fig. 3 b – Calculated mercury concentration profile in the liquid phase inside the activated carbon particle after 24 hours of the Hg^{2+} sorption process (activated carbon type DG(1-3)+S, $C_0 = 0.330 \text{ g L}^{-1}$, temp. $25 \text{ }^\circ\text{C}$)

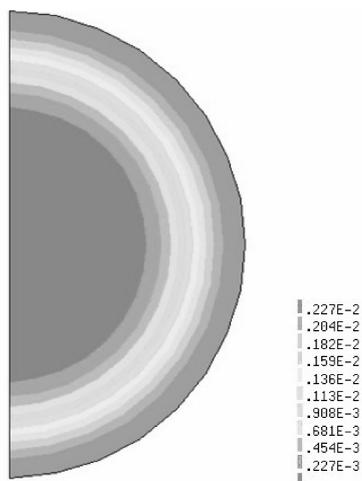


Fig. 3 c – Calculated mercury concentration profile in the liquid phase inside the activated carbon particle after 96 hours of the Hg^{2+} sorption process (activated carbon type DG(1-3)+S, $C_0 = 0.330 \text{ g dm}^{-3}$, temp. $25 \text{ }^\circ\text{C}$)

the particles of the sorbent are spheres of the same diameter and density. In order to identify the diffusion coefficients by fitting the model to experimental data the Marquardt's optimization algorithm was used.²¹

Results and discussion

In Fig. 4 and 5 the examples of sorption isotherms for Hg^{2+} and Hg^0 are shown, respectively. From these graphs it may be concluded that Langmuir model fits well the experimental data, especially in the case of ionic mercury (Fig. 4).

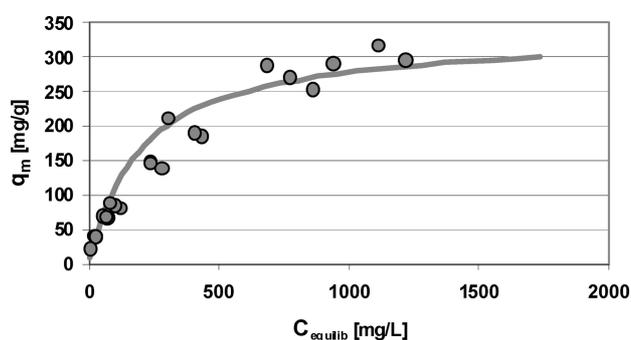


Fig. 4 – Sorption isotherm of Hg^{2+} on activated carbon DG(1-3)+S; $t = 20 \text{ }^\circ\text{C}$ (experimental points and calculated Langmuir isotherm line)

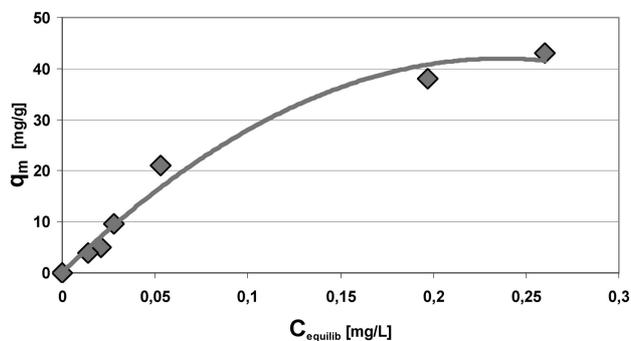


Fig. 5 – Sorption isotherm of Hg^0 on activated carbon DG(1-3)+S; $t = 20 \text{ }^\circ\text{C}$ (experimental points and calculated Langmuir isotherm line)

Fig. 6 shows that increase of the temperature has negative effect on saturation capacity of the carbons used, as it is usually in the adsorption processes, but this effect was more visible for carbons impregnated with sulfur. It seems that there may be a different mechanism of binding mercury by these two types of carbon. It is believed that due to the high affinity of mercury and sulfur, the sorption process onto sulfur-impregnated activated carbon has more likely the chemisorption nature rather than “pure” physisorption and this may be the reason of the greater influence of temperature on sorption capacity of the impregnated carbons.

The calculated Langmuir Hg^{2+} isotherm parameters and effective diffusion coefficients for all investigated types of activated carbon are collected in the table 2. According to expectations, analysis of the obtained data allowed to conclude, that activated carbons with smaller granulation, resulting obviously in higher specific surface, i.e. Merck and DGC 0.1 – 0.5, have the highest sorption capacity. However, considering liquid flow conditions in the future industrial-scale continuous fixed-bed bioreactor, the Hg adsorption capacity of the activated carbon is not the only one crucial parameter and other properties must also be taken into account. In order to lower the pressure drop in the flow-through bioreactor and to provide sufficient space for the growing biofilm the porosity of the fixed-bed must be high enough, and this may be achieved only if the carbon particles mean diameter is not too small. The value of mercury diffusion coefficient in the sorbent particles is also important, because the higher is the rate of the mass transfer process (which is obviously determined mainly by the diffusion coefficient) the shorter residence time of the liquid in the bioreactor is required, so the higher liquid flow rate may be applied – finally resulting in higher efficiency of the installation. Discussion of these contradictory arguments in relation to the investigated sorbents led to the conclusion that the activated carbon DG(1 – 3)+S seems to be the most interesting and beneficial for the particular bioremediation technology, as it has, at the same time, relatively high sorption capacity and Hg diffusion coefficient as well as the suitable granulation, assuring high porosity of the fixed-bed and low pressure drop in the liquid flow in the future industrial bioreactor.

As in our experiments two very similar activated carbon were used, differing from each other only in sulfur contents, i.e. POOL (1 – 3) and POOL (1 – 3) + S, there was a possibility to compare the influence of sulfur contained in activated carbon

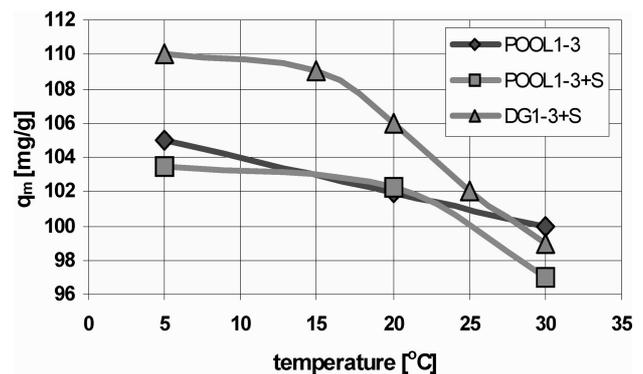


Fig. 6 – Temperature influence on the Hg sorption capacity of the selected activated carbons (experimental points and trend lines)

on its Hg sorption effectiveness. Surprisingly, as it may be seen in Table 2, the observed effect of sulfur impregnation of the carbon POOL (1 – 3) on Hg^{2+} sorption capacity was much smaller than it was shown in other publications,^{22–24} where the authors reported retention of mercury in carbons with sulfur content up to 2 – 3 times higher than in non-impregnated carbons. Comparing obtained values of the diffusion coefficient in POOL(1 – 3) and POOL(1 – 3)+S carbons (Tab. 2), it may be stated that impregnation with sulphur caused the decrease of the effective diffusion coefficient and resulted in a decrease of the adsorption process rate. The similar problem was discussed in;²⁴ the authors evaluated the chemical and physical properties of activated carbons and their dependence on sulfur impregnation. They concluded that although, in general, sulfur content improved mercury adsorption, there was no significant correlation between the mass concentration of sulfur and the equilibrium Hg adsorption capacity. It appears that micropores structure in activated carbons plays also a very important role and only the combination of sufficient number of active sulfur sites and the appropriate porous structure in a carbon particle results in large

Table 2 – Saturation capacity and effective diffusion coefficients of Hg^{2+} obtained for all investigated carbons; $t = 20$ °C

Active Carbon	POOL (1 – 3)	POOL (1 – 3) + S	POOL (0.5 – 1.6)	DG (1 – 3) + S	Merck	DGC (0.1 – 0.5)	Norit 3	DG (1 – 3) + J
q_m , mg g ⁻¹	101.7	102.3	109.7	106.1	134.6	143.8	–	103.3
$b \cdot 10^3$, dm ³ mg ⁻¹	1.1	3.2	1.5	4.9	3.9	3.1	–	3.7
$D_{Ap} \cdot 10^6$, cm ² s ⁻¹	2.08	1.33	0.81	1.23	1.64	0.59	0.27	1.19

mercury adsorption capacities. The problem is that sulfur impregnation decreases the micropores surface area (up to 50 %, according to the results presented in),²⁴ so the resulting effect of sulfur impregnation on mercury capturing ability of the activated carbons is not well understood and may be unpredictable. These issues are still in the field of our research. Nevertheless, the data presented in this paper were vital for the further investigations in a flow-through bioreactor for the mercury bio-reduction.²⁵

As it was mentioned before, the reciprocal of the Langmuir constant, $1/b$, may be considered as a sorption process equilibrium constant, K [mg L^{-1}]. Plotting the experimentally obtained values of $\ln K$ versus reciprocal of the temperature $1/T$ according to the van't Hoff equation:

$$\ln K = -\frac{\Delta H_a}{RT} + B \quad (10)$$

and then using the linear regression to the function $\ln K = f(1/T)$ one can determine the average value of adsorption enthalpy ΔH_a . For the adsorption of Hg^{2+} onto activated carbon DG (1–3)+S the average adsorption enthalpy in the temperature range of 283–303K was estimated to be -40.8 kJ/mol. This value is close to those reported in different papers for ionic mercury^{26,27} as well as for other heavy metals sorption.²⁸

In the Table 3 Langmuir parameters for the process of Hg^0 sorption onto activated carbon DG(1–3)+S at different temperatures are collected. Comparison of these data with the results obtained for ionic mercury leads to the conclusion that saturation capacity q_m for metallic mercury is at least five times smaller than for Hg^{2+} at the same temperature. There are no literature data enabling comparison of the saturation capacity of activated carbons in processes of elemental and ionic mercury sorption from aqueous solutions but from the published results for mercury removal from gas streams similar conclusions may be withdrawn. Krishnan et al.²⁹ found that the Hg^0 adsorption capacity spans over a wide range in different activated carbons and, in general, the lower the temperature the higher the adsorption capacity. Ghorishi and Gullet³⁰ also compared the adsorption capacity of different sorbents with respect to Hg^0 and HgCl_2 contained in gases, which led to the conclusion that the oxidized mercury is far more easily adsorbed than the elemental form.

The decrease of the q_m value related to the increasing temperature, obtained in this work, was unexpectedly high but plotting again the values of $\ln K$ versus reciprocal of temperature according to the van't Hoff equation we found that the average

value of adsorption enthalpy of Hg^0 onto activated carbon DG(1–3)+S is smaller than for ionic mercury and it is equal to -26.8 kJ/mol in the temperature range of 278–323K. The smaller absolute value of Hg^0 adsorption enthalpy compared to heat of ionic mercury adsorption allows to conclude that mechanisms of elemental and ionic mercury binding in sulfur impregnated activated carbon are somewhat different and in the case of mercury ions the chemisorption seems to play more significant role.

It is worth to underline that qualitatively such an effect was easy to predict, but presented quantitative data are novel and quite unique, because there are no literature data for sorption of metallic mercury on activated carbons from water solutions.

Table 3 – Influence of the temperature on Hg^0 saturation capacity of the activated carbon DG(1–3)+S

Temperature, °C	5	15	25	35	50
q_m , g g ⁻¹	71.79	35.36	21.19	17.42	6.21
b , L mg ⁻¹	8.21	4.55	11.15	24.41	26.53
$K = 1/b$, mg L ⁻¹	0.1218	0.2198	0.08968	0.04097	0.03769

Final remarks and conclusions

The aim of the presented investigations was to select the optimal activated carbon for the modified, integrated technology of bioremediation of industrial wastewater contaminated by mercury, originally developed at HZI (former GBF), Germany, and to identify the most important – for this process – parameters of the selected activated carbons, i.e. sorption capacity and diffusion coefficients in the particles. This work was the first, but important step leading to the application of the method in industrial scale. During the experiments some unique data dealing with the adsorption of elemental mercury from water solutions onto sulfurised activated carbon were obtained.

The discussion of the experimental results enables to draw the following conclusion:

– from among all the investigated sorbents the commercial activated carbon DG(1–3)+S seems to be the most interesting and beneficial for the particular bioremediation technology, as it has, at the same time, relatively high sorption capacity and Hg diffusion coefficient as well as the suitable granulation, assuring high porosity of the fixed-bed and low pressure drop in the liquid flow in the future industrial bioreactor;

– impregnation with sulfur had not great favorable influence on the equilibrium adsorption capacity of the activated carbon POOL(1-3); however sulfur addition resulted in decrease of an effective liquid diffusion coefficient in sorbent particles, which might cause decrease of the adsorption process rate in the flow-through bioreactor;

– Hg^{2+} sorption saturation capacities of the tested activated carbons were very high and all above 100 mg/g at room temperature;

– effective diffusion coefficients of Hg^{2+} ions in the particles of sorbent were 10 times smaller than diffusion coefficients in water;

– metallic mercury sorption capacity of the activated carbon DG(1–3) + S was at least 5 times smaller than obtained for Hg^{2+} at the same temperature;

– the experimentally determined average adsorption enthalpies of ionic and metallic mercury on the activated carbon DG(1–3) + S were –40.8 and –26.8 kJ/mol, respectively, which suggests that chemisorption plays significant role in the process of mercury adsorption, especially in the case of Hg^{2+} .

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Symbols used

- A – external surface area of the sorbent particle, m^2
 C_0 – initial concentration of the mercury ions in the solution, mg L^{-1}
 C_{eq} – final (equilibrium) concentration of the mercury ions in the solution, mg L^{-1}
 C_i – concentration of the mercury ions in the solution inside sorbent pores, mg L^{-1}
 D_{Ap} – intra-particle diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
 k_f – film mass transfer coefficient in a liquid phase, m s^{-1}
 m – mass of used adsorbent, g
 b – Langmuir constant, L mg^{-1}
 K – adsorption constant, mg L^{-1}
 q – amount Hg(II) adsorbed per unit mass of adsorbent, mg g^{-1}
 q_m – max. sorption capacity of used adsorbent, mg g^{-1}
 t – time, s
 V – volume of the solution, L
 ε – porosity of sorbent particle, –
 ρ_s – solid particle density, kg m^{-3}
 ΔH_a – adsorption enthalpy, kJ mol^{-1}

References

- Boening, D. W., *Chemosphere* **40** (2000) 1335–1361.
- <http://www.eurochlor.org>
- Wagner-Doebler, I., (Ed.), EU Project No. NMP2-CT-2004-505561 “Worldwide remediation of mercury hazards through biotechnology”, Final Report, HZI, Braunschweig, 2007.
- Tuzun, I., Bayramoglu, G., Yalcin, B., Basaran, G., Çelik, G., Arica, Y., *J. Env. Management* **77** (2005) 85–92.
- Holan, Z. R., Voleskey, B., Prasetyo, I., *Biotechnol. Bioeng.* **41** (1993) 819–825.
- Bae, W., Wu, C. H., Kostal, J., Mulchandani, J., Chen, W., *Appl. Env. Microbiol.* **69**(6) (2003) 3176–3180.
- Green-Ruiz, C., *Bioresource Technol.* **97** (2006) 1907–1911.
- Shaker, M., *American J. Appl. Sci.* **4**(8) (2007) 605–612.
- Kacar, Y., Arpa, C., Tan, S., Denizli, A., Genc, O., Arica, Y. M., *Process Biochemistry* **37**(6) (2002) 601–610.
- Delgado, A., Anselmo, A. M., Novals, J. M., *Water Env. Res.* **70** (1998) 370–375.
- Jeon, C., Hoell, W. H., *Water Res.* **37** (2003) 4770–4780.
- Rafique, U., Iqbal S., Rafique U., Biosorption of mercury by rice husk, in Proc. of the 7th Int. Conf. on Mercury as a Global Pollutant, June 2004, Ljubljana, Part 1, pp. 203–206.
- Ledakowicz, S., Deckwer, W-D., *Biotechnology* **3** (1993) 99–112 (in Polish).
- Wagner-Döbler, I., http://www.gbf.de/mercury_remediation1/pilotplant1.html, 2004.
- Wagner-Döbler I., Von Constain Y., Timmis K., Deckwer W-D., *Environ. Sci. Technol.* **34** (2000) 4628.
- Wagner-Döbler I., von Canstein, H., Li, Y., Leonhäuser, J., Deckwer, W-D., *Eng. Life Sci.* **4** (2003) 177–181.
- Leonhäuser, J., von Canstein, H., Wagner-Doebler, I., Deckwer, W-D., Longterm operation of a microbial mercury removing pilot plant at two chloralkali factories in Europe, in Proc. of the 7th Int. Conf. on Mercury as a Global Pollutant, June 2004, Ljubljana, Part 1, pp. 203–206.
- Wagner-Döbler I., *Appl. Microbiol. Biotechnol.* **62** (2003) 124–133.
- PARCOM Decision on Limit Values for Mercury Emissions in Water from Existing and New Brine Recirculation Chlor-alkali Plants, OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic, http://www.ospar.org/eng/html/dra/list_of_decrecs.htm (2006).
- EU Council Directive 98/83/EC of 3 Nov. 1998 on the quality of water intended for human consumption, OJ L 330, 5.12.98.
- Marquardt, D. W., *J. SIAM* **11** (1963) 431–450.
- Gomez-Serrano A., Macias-Garcia A., Espinosa-Mansilla A., Valenzuela-Calahorra C., *Wat. Res.* **32**(1) (1998) 1–4.
- Lopez-Anton, M. A., Tascon, J. M., Martinez-Tarazona, M. R., *Fuel Proc. Technol.* **77–78** (2002) 353–358.
- Hsin-Cheng H., Rood M. J., Rostam-Abadi M., Chen S., Chang R., *J. Env. Eng.* **11** (2002) 1080–1089.
- Gluszcz, P., Zakrzewska, K., Wagner-Doebler, I., Ledakowicz, S., Bioreduction of ionic mercury from wastewater in a fixed-bed bioreactor with activated carbon, *Chem. Pap.* (2007) (accepted for publication).
- Manohar, D. M., Krishnan, K. A., Anirudhan T. S., *Water Res.* **36** (2002) 1609–1619.
- Shibi, I. G., Anirudhan, T. S., *Ind. Eng. Chem. Res.* **41** (2002) 5341–5352.
- Yavuz, O., Altunkaynak, Y., Guezel, F., *Water Res.* **37** (2003) 948–952.
- Krishnan, S. V., Gullet, B. K., Jozevicz, W., *Environ. Sci. Technol.* **28** (1994) 1506–1510.
- Ghorishi, B., Gullet, B. K., *Waste Management Res.* **16** (1998) 582–593.