

**REMOVAL OF SELECTED PHARMACEUTICALS FROM AQUEOUS MATRICES  
WITH ACTIVATED CARBON**

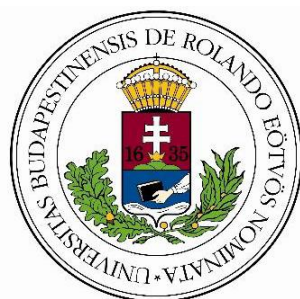
Thesis of dissertation

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## **Introduction**

Recently many studies reported the presence of emerging contaminants such as pharmaceuticals and personal care products in different aquatic systems. Presence of these contaminants in the environment has become a serious concern. Effluents from wastewater treatment plants have been identified as major sources for these pharmaceuticals in the environment due to their limited removal efficiencies. However, pharmaceutical residues find their way through the water cycle back to humans via drinking water due to their high persistence. Long-term exposure to these emerging pollutants may affect the human health and organisms in the aquatic systems.

Lately antibiotics, antidepressants, beta blockers, hormones, lipid regulators, diagnostic contrast media, antineoplastic, non-steroidal anti-inflammatory drugs (NSAIDs) such as naproxen (NPR) and diclofenac (DCL) as well as the anticonvulsant carbamazepine (CRB) among other compounds, have been detected in surface water, groundwater, wastewater, and even in drinking water at concentration levels ranging from  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$ . In 2018, the most frequently prescribed NSAIDs in Hungary were DCL and NPR. The three aforementioned active pharmaceutical ingredients (APIs) are very widely used in EU, and often occur in larger concentrations than their ecotoxicological levels all over the world.

A great variety of technologies have been developed for removal of these contaminants in water such as biological degradation, advanced oxidation and physical adsorption processes. One of the most effective methods to eliminate contaminants from the aqueous phase is adsorption onto different sorbent materials. Several novel adsorbents such as graphene, bentonite and montmorillonite clay composite, graphene oxide, (multiwall) carbon nanotubes, iron oxide nanoparticles, modified chitosan, polystyrene nanoparticles have been developed for removal of different hazardous materials. Nevertheless, adsorption onto granulated activated carbon (GAC) has been preferred for removal of pharmaceuticals from aqueous matrices.

## Objectives

The primary aim of this dissertation was to study the relationship between adsorption properties of GAC and physicochemical characteristics of pharmaceuticals under batch conditions. Another objective was to study the breakthrough curves for the target pharmaceuticals to approach operating conditions closer to the industrial application. Thus, study of adsorption of diclofenac (DCL), naproxen (NPR) and carbamazepine (CRB) from aqueous matrices onto a commercially available granulated activated carbon under both batch and continuous conditions was aimed as follows:

For batch conditions:

1. Study of the relationship between the adsorption properties (i.e. pore size and availability) of GAC and chemical characteristics of pharmaceuticals having different physico-chemical characteristics.
2. Study of the adsorption isotherms experimentally and by modeling.
3. Study of the kinetic behaviour of adsorption experimentally and by modeling.
4. Study of the temperature dependence of the adsorption process experimentally and by modelling.
5. Method proposal (i.e. semi-open system) to investigate adsorption of low-water soluble compounds (i.e. CRB) and potential interferences among the target compounds in model aqueous solutions.

For flow conditions:

1. Investigation of the effect of the initial pharmaceutical concentration, adsorbent dosage and volumetric flow rate.
2. Study of the breakthrough curves for the three pharmaceuticals using GAC in a fixed-bed column system at conditions similar to industrial application.
3. Study of the effect of flow rate and GAC mass, as well as GAC particle size on the breakthrough curve.
4. Comparison of adsorption from model solutions with secondary sewage water (SSW) using the designed fixed-bed technique.

Optimization of the adsorption parameters by application of a mathematical model for both model solutions and SSW.

## **Materials and methods**

Diclofenac sodium ( $C_{14}H_{10}Cl_2NNaO_2$ ), naproxen sodium ( $C_{14}H_{13}NaO_3$ ) and CRB ( $C_{15}H_{12}N_2O$ ) used throughout this study were of analytical grade. Different water matrixes, model solution, model sewage water and secondary sewage water were used in individual solution and mixture of the tested compounds. The secondary sewage water (SSW) bulk sample originated from the effluent stream of a wastewater treatment plant located near the capital city of Hungary. For the quantitative determination, effluent wastewater samples were filtered. For pre-concentration of the investigated APIs, 200 mg Waters Oasis HLB solid phase extraction cartridges were applied. Quantitative analysis of the compounds was achieved on a Bruker Elute ultra-high performance liquid chromatograph coupled to a Bruker Compact quadrupole–time of flight mass spectrometer (UHPLC-MS). The SSW effluent sample used for the experiments was characterized for specific electrical conductivity, pH, turbidity, anion and cation concentrations, total organic carbon and total nitrogen concentrations.

### **I. Characterization of activated carbon**

Physico-chemical characterization of GACs was conducted by nitrogen physisorption measurements which was performed at  $-196\text{ }^{\circ}\text{C}$  using an automated volumetric adsorption analyzer. Specific surface area was calculated by the BET equation. Furthermore, pore size distribution was evaluated and micropore and mesopore volumes were calculated. Also, attenuated total-reflection Fourier transform infrared spectra were recorded. Scanning electron microscopy measurements were performed on a Quanta 3D scanning electron microscope. The local elemental composition of GAC was determined by electron probe microanalysis technique. The point of zero charge of GAC was determined by using the pH drift method.

### **II. Adsorption under batch conditions**

The maximal adsorbed amounts ( $q_m$ ) were determined for DCL and NPR in a batch system. The mass of carbon, initial concentration of pharmaceuticals and volume of aqueous phase were varied between 0.05 and 0.25 g, 5 and 300  $\text{mg L}^{-1}$  as well as 50 and 500 mL, respectively. Equilibrium measurements with DCL and NPR were performed using GAC in the original presentation form, while for another set of experiments, GAC was pulverized and sieved through a 0.1 mm mesh size strainer. The resulted pulverized activated

carbon is referred to as PAC ( $d < 0.1$  mm) hereafter. The active ingredient concentration in the filtrates was determined by high performance liquid chromatography (HPLC).

Thermodynamic studies were performed at three different temperatures ( $25; 35; 45 \pm 0.1$  °C) in 100 mL of total volume using 0.1 g GAC ( $d = 0.8\text{--}1.0$  mm) for the three-component solutions. The initial concentrations were varied between 50 and 300 mg L<sup>-1</sup> for each pharmaceutical. Experimental data were evaluated by different isotherm models.

For the kinetic experiments, amounts of carbon, total volume of the suspensions and concentration of each compound were 0.5 g, 200 mL and 5 mg L<sup>-1</sup>, respectively. Larger GAC granules ( $0.8 < d < 1.0$  mm) were applied to study the individual solutions. Smaller granule size fractions ( $0.42 < d < 0.8$  mm) were also used to study adsorption from the three-component systems.

Kinetic experiments (at  $25$  °C  $\pm 0.1$  for 1 h) were performed using PAC, as well. Samples were filtered immediately and analyzed by HPLC. Data were evaluated using pseudo first order (PFO), pseudo second order (PSO), Elovich and intra particle diffusion (IPD) models.

### **III. Adsorption under flow conditions**

The experimental set-up consisted of a 10 L glass container attached to an adsorption column packed with the studied GAC with the aid of Teflon tubing. During the adsorption experiments, several glass columns differing only in diameter and height were tested. Bed height was measured after each packing and then, the mean was calculated. Flow rate was set manually before each experiment. Elution was achieved by hydrostatic pressure. In all the experiments, virgin GAC was used. Experiments were conducted at ambient temperature ( $24 \pm 1$  °C). Generally, the last 1 mL of 1 L eluate was subjected to HPLC analysis. If necessary, pH of the model solutions was adjusted to 6.1. In the case of the model sewage water samples (MSW), pH and the specific electrical conductivity were set to be the same as those of the SSW. In the optimized case, the experiments were continued until 40 L was eluted.

For study of the breakthrough curves, the SSW sample was used after spiking with the three compounds to obtain 5 mg L<sup>-1</sup> concentration for each. The initial and effluent concentrations of analytes were determined by HPLC. For the adsorption experiments, column bed contained 8 g of GAC ( $0.8 < d < 1.0$  mm). In the fixed - bed column system, the pre-column was packed with

4 g of GAC ( $1.0 < d < 1.7$  mm) and the adsorption column contained 12 g of GAC ( $0.8 < d < 1.0$  mm), flow rate was  $60 \text{ mL min}^{-1}$ . The other operating conditions were the same as in the case of the model solutions. Moreover, physico-chemical characterization of two GAC-treated spiked SSW was also determined. These two additional 1 L volume samples were taken from the effluent of the adsorption column corresponding to the  $t=16.7-33.3$  min and  $t=316.7-333.3$  min time intervals.

For another suitable aliquot of the SSW, the concentration of each analyte was 1000-fold lower. In this case, UHPLC-MS was used for the quantitative determination of the selected active ingredients after SPE separation.

By performing adsorption experiments at the  $5 \mu\text{g L}^{-1}$  concentration level, five effluent samples each of 1 L were taken corresponding to the 0-16.7 min, 66.7-83.3 min, 150-166.7 min, 233.3-250 min and 316.7-333.3 min time intervals; thus, at the end of each one 1, 5, 10, 15 and 20 L of SSW were moved through the column, respectively. The sample volume was divided into two equal aliquots and the analyte concentration was determined. As the investigated components were present in MW and SSSW matrices in very low quantities, at these experiments, checking the analytical performance of the applied methods was extremely important.

Recovery and relative standard deviation of the LC-based methods were determined by spiking the MSW and SSW samples with standard solution at two concentration levels. For quantitative determination, a five point calibration curve was applied. In the case of SPE, limit of quantification (LOQ) was calculated for the initial solutions taking into account the enrichment factor. For the mathematical calculations, the Adams-Bohart and Thomas models were applied.

## New results

T1. By applying nitrogen physisorption measurements, the commercially available Organosorb10 AA activated carbon with a mesopore volume of  $0.27 \text{ cm}^3 \text{ g}^{-1}$ , that is approximately one order of magnitude larger than those of Organosorb10 and Organosorb11, is recommended for adsorption of selected pharmaceutically active ingredients, namely diclofenac (DCL), naproxen (NPR) and carbamazepine (CRB) from aqueous matrices.

T2. By applying Organosorb10 AA in granulated (GAC) and pulverized (PAC) forms, 0.16 and  $0.33 \text{ mmol g}^{-1}$  maximal adsorbed amounts were achieved for DCL and NPR onto GAC, respectively, which increased to  $1.02 \text{ mmol g}^{-1}$  and  $1.11 \text{ mmol g}^{-1}$  when PAC was used.

T3. A semi-open system operating in batch mode with regular substrate supplementation to study adsorption of CRB as low-water soluble compound was set-up and successfully tested. By applying this system, removal efficiency was nearly 100% from model sewage water (MSW) and secondary sewage water (SSW) spiked with CRB during several substrate supplements using GAC.

T4. Adsorption onto GAC followed the Langmuir model with the best fitting in all cases ( $R^2=0.974-0.998$ ). Maximal capacity ( $q_m$ ) values derived from this model were in agreement with the maximum adsorbed amounts per adsorbent unit. Only a slight temperature dependence was observed in the experimentally determined  $q_m$  values. The determined activation energies using Dubinin-Radushkevich model for the adsorption process were 8.93, 6.62, 16.06 and  $16.20 \text{ KJ mol}^{-1}$  applying DCL-GAC, NPR-GAC, DCL-PAC and NPR-PAC, respectively. According to the model calculations performed, intra-particle diffusion is the sole rate-determining step for adsorption of CRB and NPR.

T5. Adsorption followed pseudo first order kinetics with mean rate constants of  $0.076 \text{ min}^{-1}$  for each investigated pharmaceutical in the individual solutions. However, in the three-component systems, the adsorption rate constants were 0.114, 0.125 and  $0.157 \text{ min}^{-1}$  for DCL, NPR and CRB, respectively, due to the interaction among their molecules.

T6. In the case of secondary sewage water spiked with  $5 \text{ mg L}^{-1}$  for each compound,  $60 \text{ mL min}^{-1}$  flow rate, 20 L outlet volume and  $0.05 \text{ C C}_0^{-1}$  value, breakthrough did not occur using 13.8, 14.7 and 18.3 g GAC ( $0.8 < d < 1.0$ ) amount for CRB, NPR and DCL, respectively. Breakthrough time ( $t_b$ ) increased drastically with decreasing the flow rate (e.g. to  $40 \text{ mL min}^{-1}$ ) and increasing bed height (e.g. to 187 mm), but decreased with an increase of the particle size.

T7. Due to the higher initial pH and specific electrical conductivity values, MSW provided somewhat different adsorption characteristics ( $t_b$ : 277, 206, 35.9 min for CRB, NPR and DCL, respectively) compared to the model solution ( $t_b$ : >333, 135 and 27.9 min for CRB, NPR and DCL, respectively) due to the higher organic carbon content of SSW. The desirable 90-95% removal efficiency for the investigated drugs in the flow system was achieved with the following parameter sets for precolumn and adsorption column: diameter of 12 mm, height of 140 mm, particle size of 1-1.7 mm, GAC mass of 4 g as well as diameter of 18 mm, height of 241 mm, GAC mass of 12 g, particle size of 0.8- 1.0 mm; flow rate of  $60 \text{ mL min}^{-1}$ , respectively.



### **Papers forming the basis of the dissertation**

1. M. Varga, M. ELAbadsa, E. Tatár, V.G. Mihucz. (2019). Removal of selected pharmaceuticals from aqueous matrices with activated carbon under batch conditions. *Microchemical Journal*, 148, 661–672. doi: 10.1016/j.microc.2019.104079M.
2. ELAbadsa, M. Varga, V.G. Mihucz. (2019). Removal of selected pharmaceuticals from aqueous matrices with activated carbon under flow conditions. *Microchemical Journal*, 150, 104079. doi: 10.1016/j.microc.2019.05.038.

### **Papers from earlier research work**

1. Y. El-Nahhal, M. Abadsa, S. Affifi. (2013). Adsorption of Diuron and Linuron in Gaza Soils. *American Journal of Analytical Chemistry*, 4, 94-99. doi: 10.4236/ajac.2013.47A013.
2. Y. El-Nahhal., M. Abadsa., S. Affifi. (2014). Leaching Potential of Diuron and Linuron in Gaza Soils. *American Journal of Plant Science*, 5, 4040-4049. doi: 10.4236/ajps.2014.526422

### **Conference presentations**

1. M. ELAbadsa, E.Tatár, V.G. Mihucz, M. Varga. (2018). Adsorption of selected pharmaceuticals onto granulated activated carbon. XVI Hungarian – Italian Symposium on Spectrochemistry: Technological innovation for water science and sustainable aquatic biodiversity, Budapest, Hungary.
2. M. ELAbadsa, M. Varga, E. Tatár, V.G. Mihucz. (2019). Removal of pharmaceuticals from aqueous matrices with activated carbon. 6th Sino-Hungarian Symposium on Environmental Protection, Balatonszárszó, Hungary.