Elimination of pharmaceutical residues with electrochemical methods

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Subject

Pharmaceuticals cannot be decomposed completely in wastewater treatment plants, therefore additional treatment is required.
The aim of this project is to develop a new two-step process combining adsorption on activated carbon and electrochemical degradation processes.
In the first step pharmaceutical residues are accumulated by adsorption on activated carbon. In the second step the activated carbon is regenerated electrochemically and the pharmaceuticals are partially decomposed. A boron doped diamond (BDD) electrode is used for further degradation by the formation of ozone and hydroxyl radicals. The process is shown in figure 1.
The advantages of this process are higher degradation rates of the pharmaceutical residues and the regeneration of the activated carbon.
The project is performed in cooperation with DVGW-Technologiezentrum Wasser in Karlsruhe (TZW).

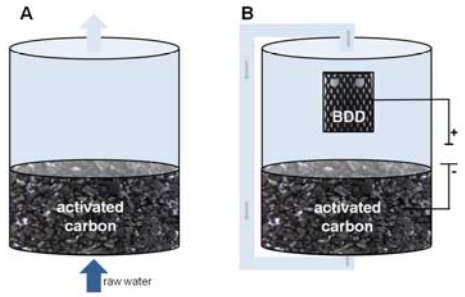


Figure 1: Scheme of the new two-step process. A: adsorption B: electrochemical desorption and decomposition

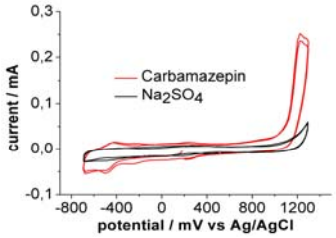
Results

The substances chosen to represent different groups of pharmaceuticals are shown in table 1.

Table 1: Pharmaceuticals chosen as model substances.

Substance	Group
Ibuprofen	anti-inflammatory drug
Diclofenac	anti-inflammatory drug
Carbamazepine	anticonvulsant drug
Sulfamethoxazole	antibiotic
Diatrizoate	radiocontrast

Electrochemical characterization



Cyclic voltammogramms (CVs) of 0,1mM of the pharmaceuticals in 0,1M Na_2SO_4 were measured on glassy carbon electrodes. A CV of *carbamazepine* is shown in figure 2.
The peaks at potentials above 1V indicate an oxidative conversion of the compounds.

Figure 2: Cyclic voltammogramms of *carbamazepine* on glassy carbon, measured in deaerated solution (20 mV/s).

Influence of the applied potential

In the case of *carbamazepine* degradation and product formation was measured as a function of the applied potential (figure 3). UV/Vis-spectroelectrochemical methods were applied. The absorbance at different wavelengths indicates *carbamazepine* degradation and product formation.

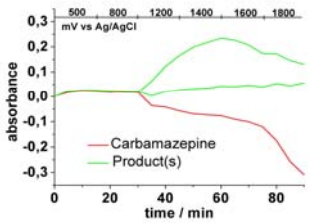


Figure 3: Decomposition of *carbamazepine* at positive potentials an glassy carbon.

The degradation of *carbamazepine* is an oxidative process (figures 2, 3), whereas no significant changes can be observed with negative polarisation.
The influence of the potential is important regarding the formation of possibly toxic products.

Influence of the BDD-electrode

Spectroelectrochemical polarization measurements were repeated with the stable x-ray contrast *diatrizoate* on BDD- and glassy carbon-electrodes with constant current density. In the case of *carbamazepine* the two electrodes behave similar. In contrast to that BDD shows a significantly better performance in the degradation of diatrizoate. BDD is therefore necessary to decompose stable substances.

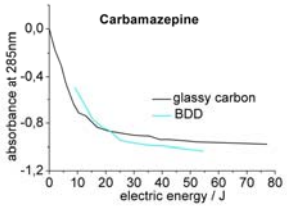


Figure 4: Degradation of *carbamazepine*. Polarized on glassy carbon (black) and BDD (blue) with 2 mA/cm² for 90 min.

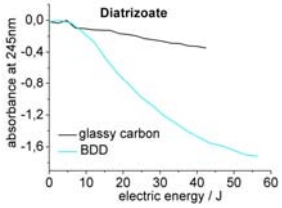


Figure 5: Degradation of *diatrizoate*.

Desorption

After adsorption of the pharmaceuticals the loaded activated carbon was polarized electrochemically in Na_2SO_4 solution. A negative potential is applied. Desorbed substances are detected by UV/Vis spectroscopy and HPLC. In figure 6 the influence of potential and counter electrode (CE) on desorption and subsequent degradation are shown in the case of *ibuprofen*.

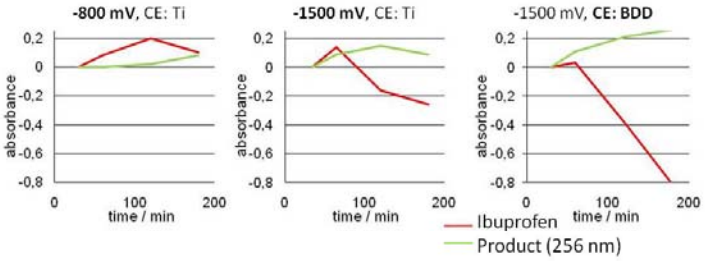
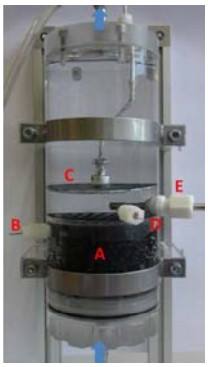


Figure 6: UV/Vis measurements during the desorption of ibuprofen from activated carbon with different potentials and materials of the counter electrode (CE). Red curve: *ibuprofen*, green curve: degradation product.

Desorption from negatively polarized activated carbon was shown for the anionic substances *ibuprofen* and *diatrizoate* as well as for the uncharged *sulfamethoxazole.*

Design of a technical cell



A technical cell was designed to combine adsorption and subsequent desorption in continuous or batch experiments (figure 7). The cell consists of an activated carbon bed with electrical contact, a BDD-counter-electrode and inlets for reference electrode and UV/Vis-probe.

Figure 7: Photograph of the technical cell.
A: Activated carbon bed
B: electrical contact for activated carbon
C: BDD counter electrode
D: reference electrode
E: UV/Vis-probe

Degradation mechanism of *diatrizoate*

The degradation mechanism of the stable x-ray contrast *diatrizoate* was studied by cyclic voltammetry. CVs on glassy carbon exhibit three peaks in the cathodic region at -1100mV, -1500mV and -1700mV vs. NHE (figure 8).
They are assumed to be due to the stepwise de-iodination of *diatrizoate*.

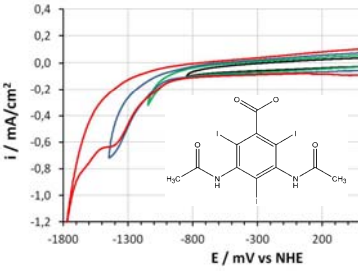


Figure 8: CVs of diatrizoate on glassy carbon (50mV/s, deaerated solution).

Further experiments are carried out to reveal the degradation mechanism during anodic and cathodic polarization.