FACULTY OF **BIOSCIENCE ENGINEERING**

Removal of Cytostatic Platinum Compounds and Recovery of Precious Metal from Aqueous Wastestreams

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Platinum release and environmental effects

Over the last decades, a strong antropogenic increase in platinum concentrations in the environment is observed. While catalytic converters used in cars and industry contribute to elevated levels in vegetation and soils, hospitals intensely discard platinum from their effluents to surface waters. [1]

Since the discovery of its cytostatic properties by Rosenberg, cisplatin and other platinum coordinating compounds such as carboplatin and more recently oxaliplatin are extensively used in chemotherapy for cancer treatment. After ingestion and interaction with DNA, the drugs are biodegraded and excreted by patients through urine – either in hospital or at home - to remain mostly untreated. [2]

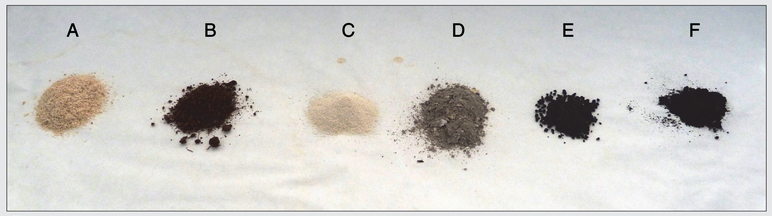

Figure 1. *Biomaterials used as sorbent: cellulose (A), peat (B), chitosan (c), wood ash (D), biochar (E) and active carbon (F) as a reference material.*

POTENTIAL OF BIOMATERIALS

Biomaterials are ubiquitous distributed over the world and ready available with equal performance. They show a promising potential as sorbent for pollutants from wastewaters. [3] The precious metal containing material can be separated from solution as a solid and be processed and valorised afterwards .

In a screening step, several natural wood-based materials and dried microalgal biological flocs (MaB) [4] have been tested for their sorption efficiency towards cytostatic platinum compounds (CPC).

Materials and Methods

- Sorption experiments were carried out in initial 100 µg L^{-1} Pt medium with L/S ratio of 100 in PE recipients and subjected to 0.45 µm filtration and digestion in a microwave oven prior to analysis.
- Real effluent samples were taken at water treatment site of AZ Maria Middelares hospital (Ghent – 554 hospital beds), both prior and post alumina coagulation-flocculation.
- Total platinum concentrations were subsequently analysed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) with an established detection limit of 5 ng L^{-1}.
- To distinguish between different platinum compounds, speciation-analysis was performed on HPLC-ICP-MS using Discovery® HS F5 column with 10 mM ammonium acetate in 2% methanol mobile phase followed by ^{195}Pt mass detection. [5]

Results and Discussion

SORPTION CAPACITIES

Individual tests of the proposed biomaterials for platinum compounds revealed important differences, as in Figure 2. The organic character of oxaliplatin and carboplatin generally resulted in lower sorption capacities, whereas the inorganic and ionic species of platinum (IV) chloride and cisplatin showed easiest sorption.

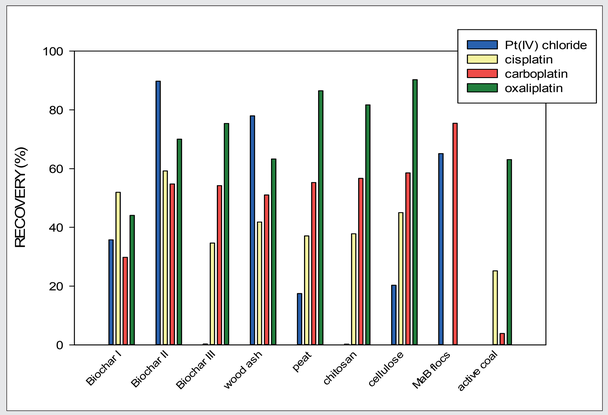

Figure 2. *Recoveries of elemental platinum after 24 hour mixing with biomaterials in 9 different batches. Biochars 1, 2 and 3 underwent increasing pyrolysis times originating from identical wood sample. Highest overall platinum removal is shown by biochar 1 and wood ash. Experiment performed in triplicate.*

KINETICS OF SORPTION

Differences in 24 hour sorption efficiencies are tempered by the occurring sorption mechanism of each sorbent. Chitosan and wood ash reached equilibrium conditions after less than 2 hours.

SPECIATION-ANALYSIS

Total platinum presence in hospital effluent was observed as 52 ± 8 ng L^{-1}. Speciation-analysis was performed using external standard series (Figure 3). Detection limits in the chromatographic method are responsible for a difficult direct speciation of CPC in hospital samples since matrix effects in wastewater and urine samples led to an increased noise level.

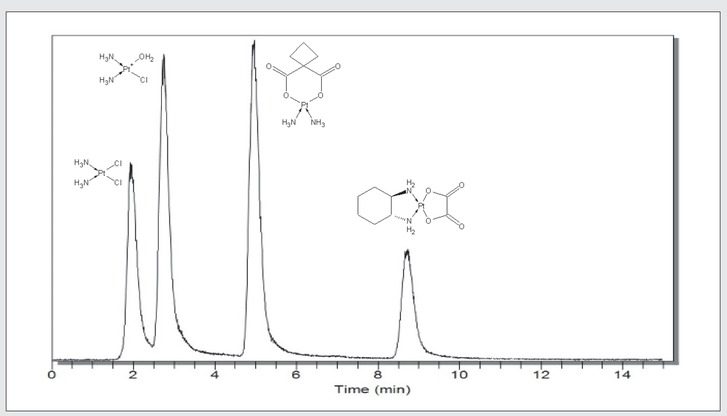

Figure 3. *Chromatogram of cancerostatic platinum compound (CPC) standards. Separation of 214 µg L^{-1} cisplatin (3.12 min), 245 µg L^{-1} monoaquacisplatin (2.75 min), 325 µg L^{-1} carboplatin (4.94 min) and 196 µg L^{-1} oxaliplatin (8.73 min) is obtained.*

Conclusions

SORPTION ON BIOMATERIALS

- Removal and detoxification of cytostatic drugs is of critical importance for the environment and can be associated with economic benefits.
- The individual screening of platinum component sorption to biomaterials allows to develop mechanistic insights and specific removal strategies based on optimal performances.
- Although large variations between platinum species, good overall sorption capacities were found for biomaterials (Table 1). Especially biochar (59.6% relative platinum removal) and chitosan (55.9%) excel.

Table 1. *Relative platinum removal of biomaterials, calculated as the average removal of 4 platinum species under described experimental conditions .*

SORBENT	RELATIVE REMOVAL (%)	SORBENT	RELATIVE REMOVAL (%)
Biochar 1	59.6	cellulose	46.5
Biochar 3	58.9	Wood ash	41.5
Chitosan	55.9	Biochar 2	31.5
Peat	50.9	MaB flocs	29.7

- Taking into account kinetic information, wood ash and chitosan are able to sorb fast, possibly because of the smaller particle size.

SPECIATION-ANALYSIS

- Dissolution of cisplatin powder in 20 mM chloride revealed the ligand exchange with water and formation of monoaquacisplatin within instants. Other compounds did not show initial degradation products.
- The quantification of CPC species with HPLC-ICP-MS method is subjected to a detection limit of 50 µg L^{-1}. Challenges are to lower this concentration in order to match actual conditions.

OUTLOOK

- The synthesis of biomaterials and effect of modifications with functional groups will be investigated and may highly influence the sorption process.
- In understanding the complete loop of platinum contamination, it is important to track the sources. This will be done upon additional sampling of treated patient's urine.

References and Acknowledgements

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