Rose bengal and methylene blue dyes are poor proxies for PFOA-sorption to biochar

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Abstract

# Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a large group of synthetic chemicals … One of the most common PFAS found in soil and water is perfluorooctanoic acid (PFOA), PFOA is used as an emulsion stabilizer in the production of fluorinated polymers and elastomers such as GoreTex, Teflon and. PFOA is listed under the Stockholm Convention as a persistent organic pollutant (POP) and its manufacture and use was banned from 2020.

Sorengård concludes that dyes can be used as proxies for PFAS sorption. A dye test is a cost and time-effective way to evaluate the expected sorption capacity/affinity for PFAS of a new sorbent and would deem a helpful tool when commercial production of biochar “takes off” so that the biochar manufacturer can quickly report variations in each batch of sorbent products and the sorbent quality when a new feedstock is tested.

In this study, the correlation between sorption of PFOA and two high-purity dyes to 24 different biochar adsorbents was investigated in batch sorption experiments. The objective of the study was to verify if sorption of dyes are suitable as proxy to predict sorption of PFOA to biochar.

# Materials and methods

## Biochar sorbents

### Biochars

Nine feedstocks were selected for biochar production: cardboard, clean wood chips, two digested sewage sludges, dewatered sewage sludge, food waste reject, garden waste, limed sewage sludge, and waste timber. All feedstocks were waste-based except for the commercially available clean wood chips (CWC) made from softwood timber mainly of spruce and pine (Hallingdal Trepellets, Ål, Norway). The feedstocks were dried (waste-based feedstocks) or shredded (CWC) and compressed into 8 mm pellets before pyrolysis.

The biochars were produced by slow pyrolysis using two different pyrolysis technologies: microwave assisted pyrolysis (MAP) and Biogreen© at temperatures between 500-800 ˚C and three residence times (Table 1). A biochar sub-sample (100 g) was taken by random grab-sampling from the bulk volume (~5 kg). The biochars were crushed using a ball mill (Retsch ISO 9001) and sieved into fine-powdered biochar (<2 mm). A total of 24 biochars were selected as sorbent materials for the batch test experiments.

Table 1 Feedstocks, pyrolysis temperatures, residence times, and pyrolysis technologies selected for the batch test experiments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Biochar ID** | **Pyrolysis temperatures (˚C)** | **Residence time (min)** | **Pyrolysis technology** | **Feedstock** |
| CB-MAP | 650 | 90 | MAP | Cardboard |
| CWC-BC | 600, 700, 750 | 20 | Biogreen | Clean wood chips |
| DSS-1-BC | 600, 700 | 20 | Biogreen | Digested sewage sludge |
| DSS-1-MAP | 650 | 90 | MAP | Digested sewage sludge |
| DSS-2-BC | 500, 600, 700, 800 | 20 | Biogreen | Digested sewage sludge |
| DWSS-BC | 600, 700, 800 | 40 | Biogreen | Dewatered sewage sludge |
| FWR-BC | 800 | 20 | Biogreen | Food waste reject |
| GW-BC | 500, 600, 800 | 20 | Biogreen | Garden waste |
| GW-MAP | 650 | 90 | MAP | Garden waste |
| LSS-BC | 600 | 20 | Biogreen | Limed sewage sludge |
| WT-BC | 600, 700, 800 | 20 | Biogreen | Waste timber |
| WT-MAP-A | 650 | 90 | MAP | Activated waste timber |

## Analytical PFAS standards and dyes

Perfluorooctanoic acid (PFOA, C8) was selected as target analyte for the batch sorption test experiments. A PFOA stock solution was prepared from pure PFOA salt acquired from Sigma Aldrich™ that was dissolved in methanol.

Methylene blue and rose bengal were selected as dyes based on the results reported in Sörengård et al. 2019. Details on MW, solubility, structural and chemical formulae, ionic charge, and molecular size of the dyes are provided in the SI.

Table 2 Details on the target analytes tested, including CAS number, structural formula, chemical formula, class, molecular weight (MW), and solubility constant (Sw).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Compound/**  **CAS no.** | **Structural formula** | **Chemical formula** | **Class** | **MW (g/mol)** | **Sw (g/L)** |
| Methylene blue/  61-73-4 | Methylene Blue | C16H18ClN3S - PubChem | C16H8N2Na2O8S2 | Pheno-  thiazine | 319.851 | 43.6 |
| Rose bengal/  632-69-9 | rose bengal (photoactivated) | C20H4Cl4I4O5 | ChemSpider | C20H4Cl4I4O5 | Xanthene | 1017.628 | N/F |
| Perfluoro-octanoic acid/335-67-1 |  | C8 HF15O2 | Perfluori-nated carboxylic acid (PFCA) | 214.04 | 3.4 |

Table 3 Start concentration, start absorbance, calibration curve equation, and max absorbance of the dyes tested. The x-value in the calibration curve equation is the absorbance and the y value is the dye aqueous concentrations.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Dye** | **Start concentration (mg/L)** | **Start absorbance** | **Calibration curve equation** | **Maximum absorbance (λ) (nm)** |
| Methylene blue | 10 | 1.9 | y = 25.953x - 1.9764  *R2* = 0.99 | 662 |
| Rose bengal | 50 | 1.6 | y = 5.4014x - 0.0348  *R2* = 0.99 | 564 |

SI

## Batch experiments

Batch sorption tests were prepared with a liquid-to-solid mass ratio (L/S) of 500 for biochar and water solution in 50 mL polypropylene (PP) centrifuge tubes. The different batch test categories prepared were: 1) biochar spiked with PFOA at five concentrations (1, 10, 100, 1000, 5000 µg/L), 2) biochar spiked with methylene blue at 10 mg/L in triplicate, and 3) biochar spiked with rose bengal at 50 mg/L in triplicate. The starting concentrations of the dyes were selected based on the sensitivity of the quantitative analysis. Special attention was paid to ensure that the concentrations spiked were below the critical micelle concentrations (CMC) of the different PFOA46,47 and that the samples contained <1% MeOH. Negative blanks were prepared in triplicate. Spiked blanks were prepared at each of the five concentrations, whereof the lowest concentration point was prepared in triplicate (1 µg/L).

The PFOA samples were shaken end-over end (9 rpm) at room temperature (23°C) for 14 days, which is considered sufficient for equilibration to be achieved45. The dye samples were agitated on a shaking table (160 rpm) for seven days, according to the methods described in Sorengård et al. 2019. After shaking, the PFOA samples were filtered through a 0.45 µm Minisart® regenerated cellulose syringe filter into PP tubes.32 and sent to the commercial laboratory, Eurofins, and analyzed for according to CENXXXX. The dye samples were left to settle for 24 hours and the supernatants were carefully decanted and analyzed with a Thermo Scientific™ Orion™ AquaMate 8000 UV-Vis spectrophotometer using a 5-point calibration curve.

## Data analysis

Statistical analyses were carried out using the ggplot2 package49 in RStudio IDE (2022.02.0-443), R v.4.1.2.

As the sorption of PFCAs to biochar was non-linear16, the Freundlich equation was used to describe the sorption isotherms50,51 such that:

|  |  |
| --- | --- |
|  | ( 1 ) |

where *Cs* is the sorbed PFOA concentration in µg/kg, *KF* is the Freundlich distribution coefficient in (µg/kg)/(µg/L)nF, *nF* is the dimensionless coefficient of non-linearity, and *Cw* is the equilibrium aqueous PFOA concentration in µg/L. As the sorbed PFAS concentration was not analyzed directly, *Cs* at equilibrium was calculated assuming 100% mass balance.

For the batch tests with dyes prepared in triplicate, distribution coefficients (*Kd*) between biochar (*Cs*) and filtered water (*Cw*) were calculated assuming a linear sorption model by dividing the mean *Cs* by the mean *Cw*:

|  |  |
| --- | --- |
|  | ( ) |

# Results and discussion

## Correlation of sorption behavior of PFOA and dyes

The Spearman’s rank correlation test showed that the correlation between sorption of the dyes and PFOA was low. Spearman’s ρ values for methylene blue and rose bengal were 0.55 and 0.53, respectively, although the correlations were significant (p < 0.05) (Table 5). Figure 1 shows the relationship between the Kd values for methylene blue, rose bengal and PFOA (extrapolated to 1 mg/L from isotherm).

The regressions are significant (p<0.05) but prediction intervals are wide (mean PI = ± 2.3 log KF; (Figure 2). Since the distribution coefficient, log KF is logarithmic, prediction within two log units is relatively poor.

Hvorfor ikke isotherm for fargetestene

Forskjell mellom konsentrasjonsområdene for å få riktig absorbans, kan ikke interpolere/ekstrapolate isotermene

Table 4 Freundlich distribution coefficients (log *KF*) in units of (µg/kg)/(µg/L)*nF,* non-linearity coefficients (*nF*) with standard deviations and the corresponding linear regression coefficients for the sorption isotherms (n=5). Uncertainty is represented by the 95% confidence interval for the slope and intercept of the regression line.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample ID** | **Sample description** | **log *KF*** | | | ***nF*** | | | ***r2*** | ***p-value*** |
| CWC-600 | Clean wood chips 600 °C |  |  |  |  |  |  |  |  |
| CWC-700 | Clean wood chips 700 °C | 3.84 | ± | 0.26 | 0.51 | ± | 0.12 | 0.86 | 0.02 |
| CWC-750 | Clean wood chips 750 °C | 4.54 | ± | 0.20 | 0.59 | ± | 0.10 | 0.92 | 0.01 |
| FWR-800 | Food waste reject 800 °C | 3.35 | ± | 0.12 | 0.69 | ± | 0.06 | 0.98 | 0.001 |
| DSS1-600 | Digested sewage sludge 1 600 °C | 3.27 | ± | 0.19 | 0.68 | ± | 0.08 | 0.96 | 0.004 |
| DSS1-700 | Digested sewage sludge 1 700 °C | 4.30 | ± | 0.11 | 0.65 | ± | 0.06 | 0.98 | 0.001 |
| GW-500 | Garden waste 500 °C | 1.66 | ± | 0.24 | 1.08 | ± | 0.09 | 0.99 | 0.01 |
| GW-600 | Garden waste 600 °C | 2.48 | ± | 0.08 | 0.73 | ± | 0.04 | 0.99 | 0.004 |
| GW-800 | Garden waste 800 °C | 4.56 | ± | 0.22 | 0.60 | ± | 0.11 | 0.91 | 0.01 |
| DSS2-500 | Digested sewage sludge 2 500°C | 2.61 | ± | 0.02 | 0.84 | ± | 0.01 | 1.00 | 0.0002 |
| DSS2-600 | Digested sewage sludge 2 600 °C | 4.28 | ± | 0.09 | 0.61 | ± | 0.04 | 0.99 | 0.001 |
| DSS2-700 | Digested sewage sludge 2 700 °C | 4.69 | ± | 0.15 | 0.65 | ± | 0.08 | 0.96 | 0.004 |
| DSS2-800 | Digested sewage sludge 2 800 °C | 5.69 | ± | 0.17 | 0.79 | ± | 0.08 | 0.97 | 0.002 |
| DWSS-600 | Dewatered sewage sludge 600 °C | 4.10 | ± | 0.17 | 0.60 | ± | 0.08 | 0.95 | 0.01 |
| DWSS-700 | Dewatered sewage sludge 700 °C | 5.62 | ± | 0.23 | 0.76 | ± | 0.11 | 0.94 | 0.01 |
| DWSS-800 | Dewatered sewage sludge 800 °C | 6.72 | ± | 0.22 | 0.89 | ± | 0.11 | 0.97 | 0.01 |
| LSS-600 | Limed sewage sludge 600 °C | 2.56 | ± | 0.11 | 0.89 | ± | 0.06 | 0.99 | 0.005 |
| WT-600 | Waste timber 600 °C |  |  |  |  |  |  |  |  |
| WT-700-1 | Waste timber 700 °C | 3.88 | ± | 0.20 | 0.55 | ± | 0.09 | 0.92 | 0.01 |
| WT-700-2 | Waste timber 700 °C | 3.86 | ± | 0.17 | 0.58 | ± | 0.08 | 0.95 | 0.01 |
| WT-700-3 | Waste timber 700 °C | 3.82 | ± | 0.27 | 0.52 | ± | 0.13 | 0.85 | 0.03 |
| WT-800 | Waste timber 800 °C | 4.13 | ± | 0.21 | 0.58 | ± | 0.10 | 0.92 | 0.01 |

Table 5 Correlation coefficients (R-squared) and p-values for the correlations between sorption of the two dyes (methylene blue and rose bengal) and PFOA for *n* = 18 biochars.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | rose bengal | methylene blue |
| Linear model | p-value | 0.0001266 | 0.0001914 |
| R-squared | 0.4564 | 0.4373 |
| Ranked linear model | p-value | 0.0001266 | 0.0002038 |
| R-squared | 0.4564 | 0.4343 |
| Spearman correlation | p-value | 0.000112 | 0.0002038 |
| rho | 0.6959201 | 0.6766746 |

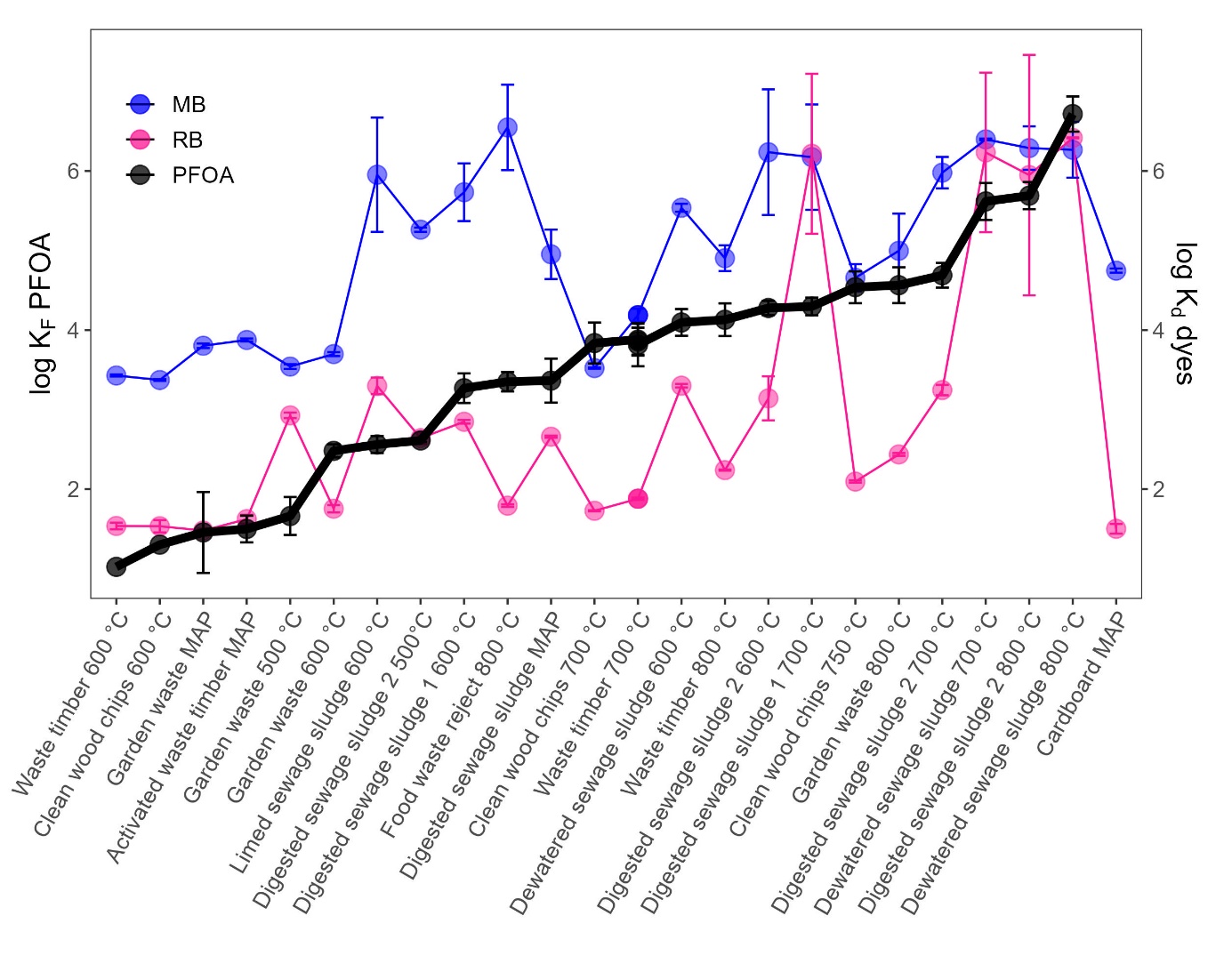


Figure 1 Mean log *Kd* values in L/kg for methylene blue (MB, n=3), and rose bengal (RB, n=3) to the biochar adsorbents. The black dot-connected line represents the log *Kd* values for PFOA at 1 mg/L that have been extrapolated from the isotherms using the conversion equation, log *Kd* (1 mg/L) = log *Kd* (1 µg/L) – 3\*(1-*nF*). The error bars represent the +/- standard deviations.

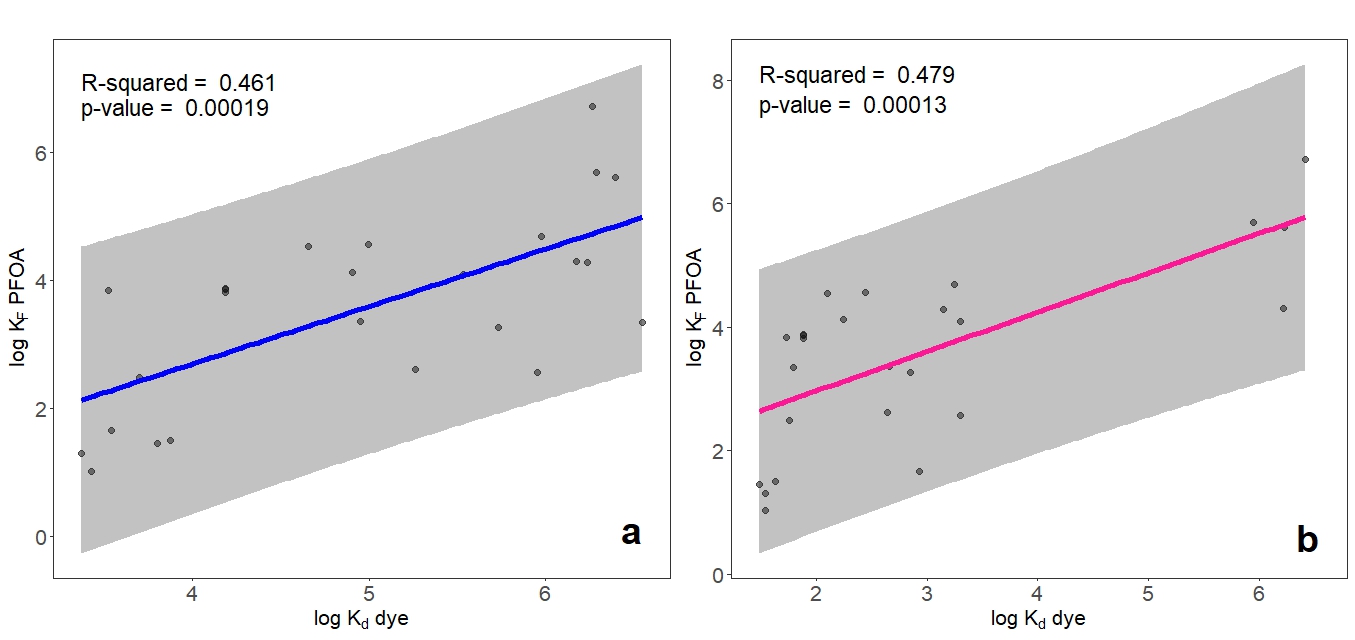


Figure 2 linear model showing the correlation between log KF for PFOA and log Kd for the dyes, (a) methylene blue and (b) rose bengal. The grey ribbons represent the 95% prediction intervals.

# Conclusion

We conclude that

# Supporting Information

If any…

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