Synthesis of granular activated carbon from biomass and correlation of its sorption properties with the pore space characteristics

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Objectives

- **Evaluation of the adsorption capacity of granular activated carbons (GACs)** prepared from agricultural waste (AW): banana peel (BP) activated carbon (BPAC) (adsorption of mixture of the cationic Methylene blue (MB) and the anionic Orange G (OG) dyes), coffee waste (CW) activated carbon (CWAC) (adsorption of the polycyclic aromatic hydrocarbon (PAH) phenanthrene (PHE)).
- **Analysis of the pore structure properties of the adsorbents** with Scanning-Electron-Microscopy (SEM), nitrogen sorption isotherms, and mercury intrusion porosimetry (MIP), Raman and ATR-FTIR spectroscopy.
- **Simulation of the dynamics of pollutant sorption on the pore structure of GAC** with the multi-compartment model so that the external and internal mass-transfer coefficients along with the effective pore and surface diffusion coefficients were estimated with inverse modeling.
- **Correlation of the rate-controlling step of sorption process with GAC characteristics, pollutant type, and sorption conditions** through the simulation of sorption dynamics and the determination of sorption isotherms and kinetics (Langmuir, Freundlich, Sips, 1st order, 2nd order, intraparticle diffusion models) with batch tests.
- **Investigation of the potential to regenerate the adsorbents** by the green and economic technology of cold atmospheric plasma (CAP) and the various types of GAC.

Proof of concept

Target pollutants

Dyes (Methylene blue, Orange G)

Polycyclic aromatic hydrocarbons (Phenanthrene)

Harmful for the ecosystem and human health, carcinogenic, mutagenic

Reuse

Novel green, efficient and economic advanced oxidation process → solid waste and wastewater management, material modification, medicine, and agriculture.

Adsorbent regeneration with **Cold Atmospheric Plasma (CAP)**

Adsorption

Cost effectiveness
Simple operation
High efficiency
Selectivity

Economic & environmental sustainability

Adsorption + Cold Atmospheric Plasma regeneration

Two-step strategy for the remediation of wastewater from various types of pollutants

Resolution of the issue of the valorization or disposal of the saturated adsorbents

Low-cost adsorbents

Agricultural waste (AW)

Coffee → 6 million tons/year (the most popular beverage worldwide with the volume of husk, bean, and spent ground residues being enormous)

Banana → 114 million tons/year (consumed globally as a food or used to produce a variety of products in the cosmetics or textile industries)

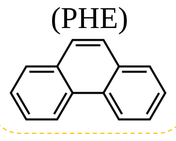
Chemical and/or physical treatment

Activated carbon (AC) from AW

large surface area, high porosity, functional groups, selectivity

Methodology

Phenanthrene (PHE)



Preparation of coffee waste activated carbons

Coffee residues

Mixed with distilled water in ratio 1:10, stirred for 1 hour, filtered, oven dried

Coffee waste (CW)

NaOH

H_3PO_4

Pyrolysis at 800 °C for 1 hour under N_2 flow

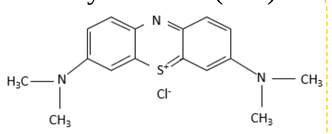
Washed under vacuum with HCl/NaOH and distilled water until neutral pH

CWAC

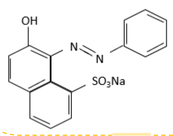
- CWAC-800
- CWAC-NaOH-800
- CWAC-H_3PO_4-800

Preparation of banana peel activated carbons

Methylene blue (MB)



Orange G (OG)



Banana peels

Washed/ Dried/ Crashed/ Sieved (125-500 μm)

Untreated banana peels (BP)

NaOH

H_3PO_4

Pyrolysis at 500, 600, 700 °C for 1 hour under N_2 flow

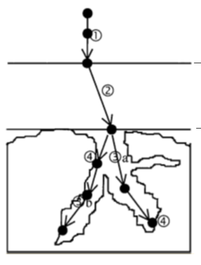
Washed under vacuum with HCl/NaOH and distilled water until neutral pH

Mixture

BPAC

- BPAC-700
- BPAC-H_2SO_4-700
- BPAC-NaOH-700
- BPAC-NaOH-600
- BPAC-NaOH-500

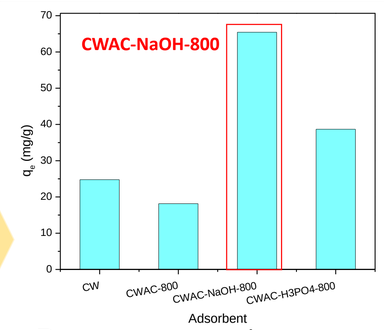
Steps governing the dynamics of pollutant sorption on granular activated carbon (GAC)



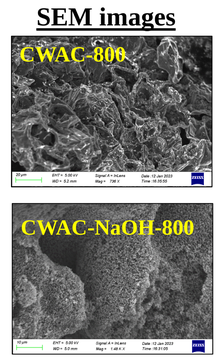
Position	Phenomenon	Coefficient
Bulk of solution	① Diffusion/Convection	Fast
Outer layer	② External Mass Transfer	k_f
GAC particle	③a Porous Diffusion	D_P
	③b Surface Diffusion	D_F
	④ Adsorption	Instantaneous

Adsorption on activated carbons

Selection of the most efficient AC for the removal of PHE

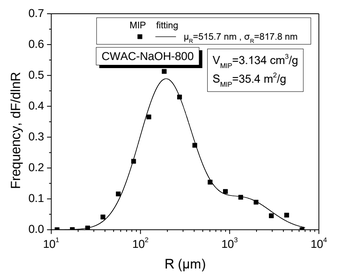


SEM images

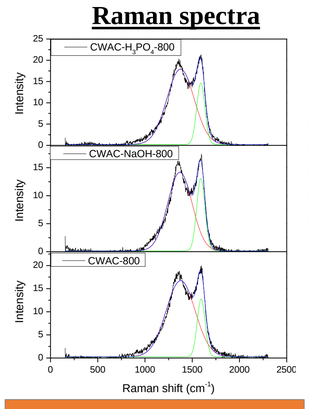


Characterization of adsorbents

Mercury intrusion porosimetry



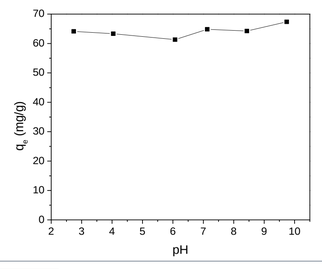
Raman spectra



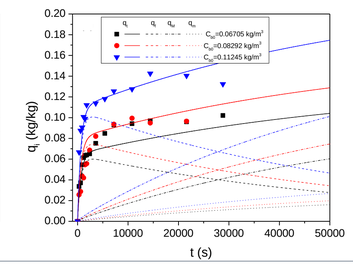
Pore space properties

Adsorbent	S_{BET} (m^2/g)	$V_{P,LN2}$ (cm^3/g)	Mean radius μ_R (nm)
CW	0.25	0.0024	-
CWAC-800	159.0	0.0604	56.70
CWAC-H_3PO_4-800	167.5	0.0815	61.0
CWAC-NaOH-800	676.5	0.415	43.10

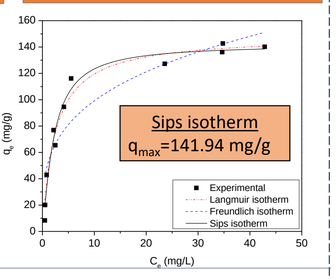
Effect of pH



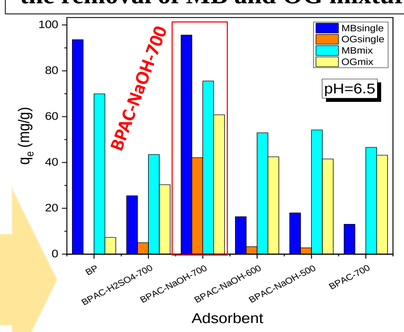
Simulation of sorption dynamics



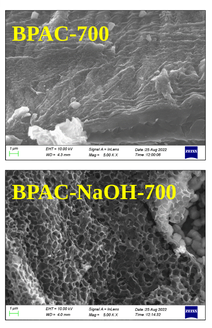
Adsorption isotherms



Selection of the most efficient AC for the removal of MB and OG mixture

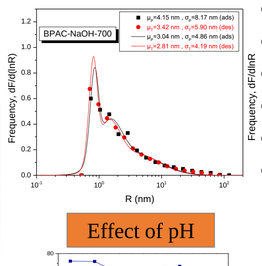


SEM images

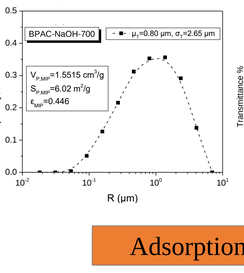


Characterization of adsorbents

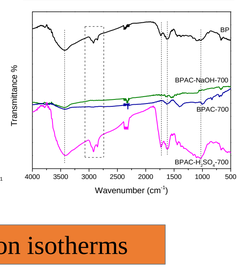
N_2 isotherms-Pore size distribution



Mercury intrusion porosimetry



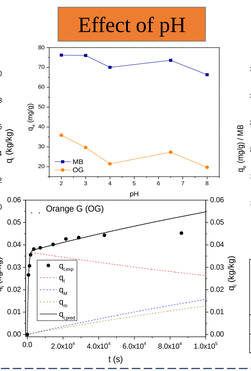
ATR-FTIR spectra



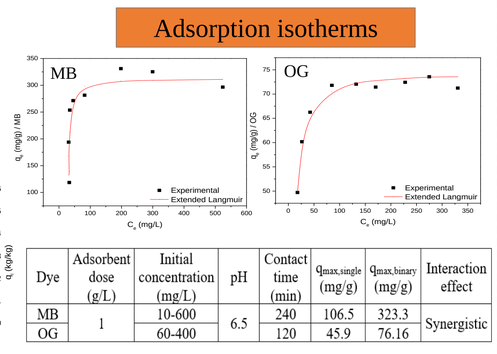
Pore space properties

Adsorbent	S_{BET} (m^2/g)	$V_{P,N2}$ (cm^3/g)	μ_P (nm) - Adsorption	μ_T (nm) - Desorption
BP	0.0	0.005	-	-
BPAC-700	4.633	0.025	28.70	23.46
BPAC-NaOH-700	524.027	0.262	3.04	2.81
BPAC-NaOH-600	388.166	0.341	19.00	12.77
BPAC-NaOH-500	282.753	0.260	18.51	12.40
BPAC-H_2SO_4-700	157.104	0.092	13.00	12.17

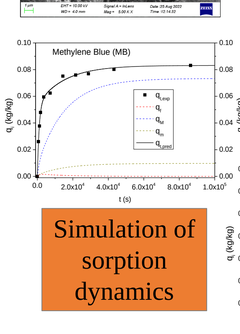
Effect of pH



Adsorption isotherms



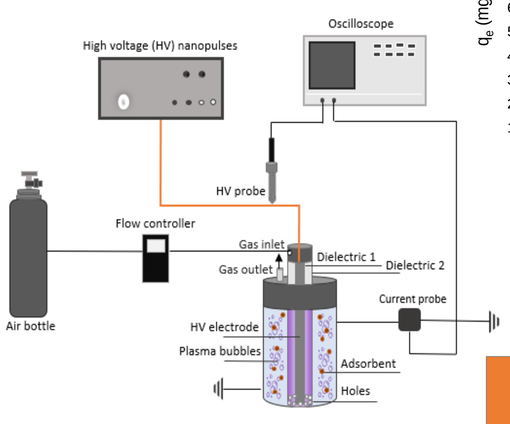
Simulation of sorption dynamics



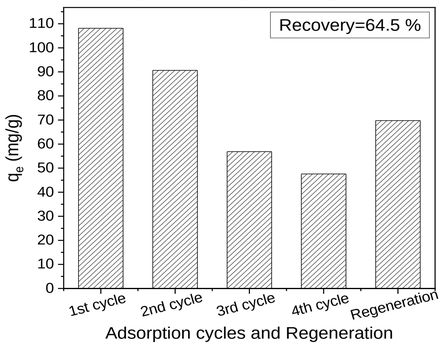
Dye	Adsorbent dose (g/L)	Initial concentration (mg/L)	pH	Contact time (min)	$q_{max,single}$ (mg/g)	$q_{max,binary}$ (mg/g)	Interaction effect
MB	1	10-600	6.5	240	106.5	323.3	Synergistic
OG		60-400		120	45.9	76.16	

Cold atmospheric plasma (CAP) regeneration

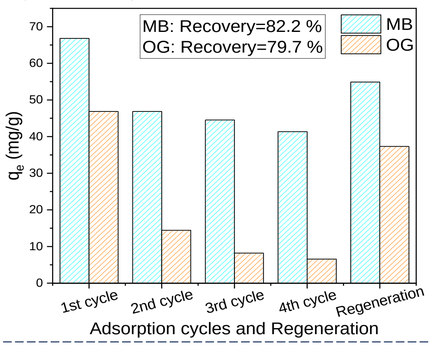
Experimental setup of CAP-bubbling system with dielectric barrier discharge (DBD) reactor



Reuse and CAP regeneration of CWAC-NaOH-800



Reuse and CAP regeneration of BPAC-NaOH-700



Conclusions

✓ **Most efficient adsorbents →** Banana peel (Methylene blue + Orange G adsorption) and coffee waste (Phenanthrene adsorption) pre-treated with NaOH and pyrolyzed at 700 and 800 °C, respectively (enhancement of the specific surface area (S_{BET}) and creation of a well-developed porous network with different pore shapes and sizes).

✓ **Simulation of sorption dynamics with the multi-compartment model**

BPAC-NaOH-700 → the preference of BPAC-NaOH-700 to MB dye sorption leads to the coverage of the internal pore surface with this compound and its depletion from the solution, while the OG dye sorption is limited to the external particle surface with coverage of a small fraction of the internal pore surface, due to the very slow rates of pore and surface diffusion.

CWAC-NaOH-800 → at late times, most of the adsorbed mass of PHE has been transferred to meso-/macro-porosity while the PHE concentration adsorbed on the micro-pores might become discernible at very late times.

✓ **Sorption mechanism**

BPAC-NaOH-700-MB+OG → push-pull mechanism of self-aggregated dimers of oppositely charged cationic and anionic dyes.

CWAC-NaOH-800-PHE → π–π interactions between hydrophobic PHE rings and graphene layers of CWAC-NaOH-800.

✓ **Cold atmospheric plasma regeneration**

Very good reusability of both adsorbents and values of the recovery of the adsorption capacities.

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