PREPARATION, CHARACTERIZATION AND APPLICATION OF HIGH SURFACE AREA ACTIVATED CARBONS AS ADSORBENT FOR REMOVAL OF ORGANIC COMPOUNDS FROM AQUEOUS EFFLUENTS

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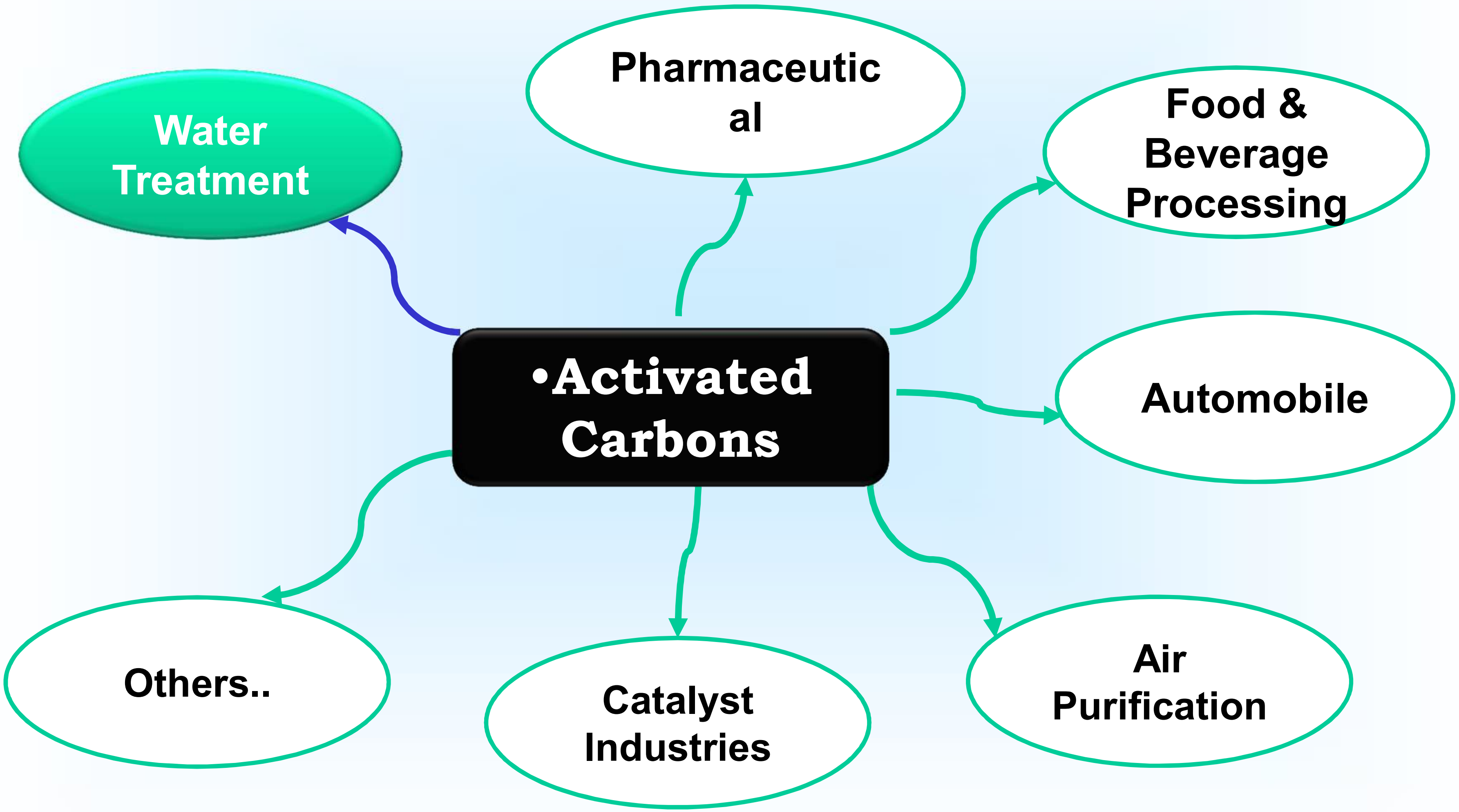
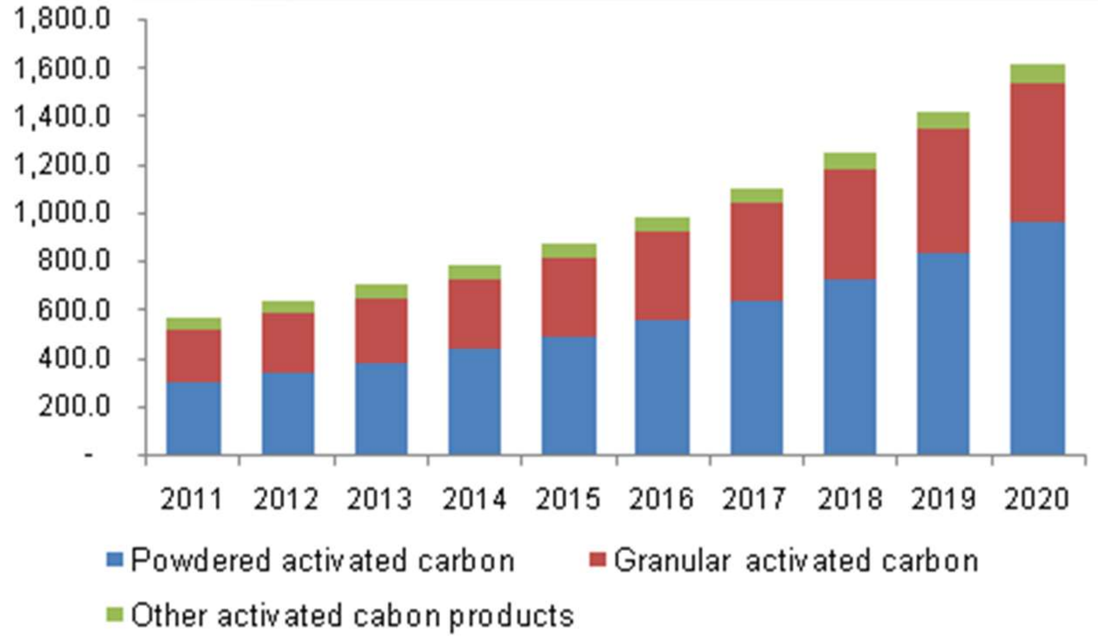
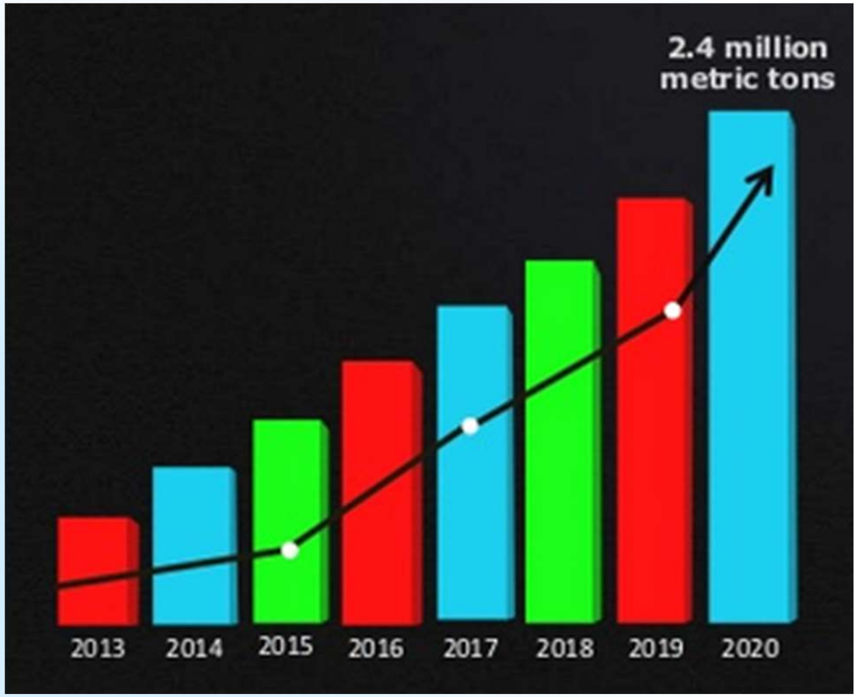
•Activated Carbon End-use Outlook



Annual Production of activated carbon



Consummation of Activate Carbon



This fact has inflated the price of activated carbon on the market

In 2020 the consummation of activated carbon will attain 2.4 million of m^3

The performance of activated carbon as adsorbent

These properties are directly related to the physical and chemical properties of the precursor material, the type of the production method and the production conditions

Surface areas;

Pore volumes;

Pore size distribution

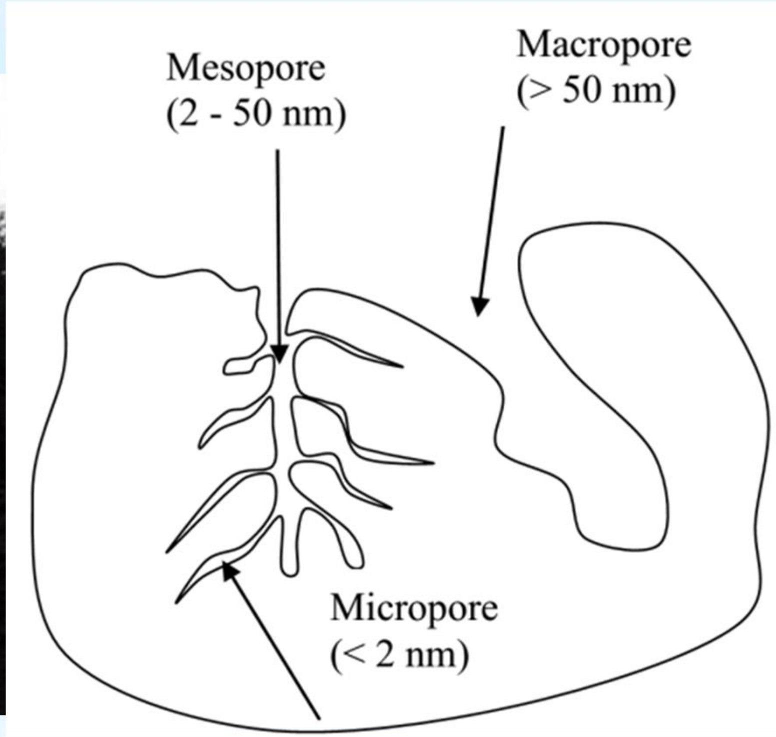
Surface Chemistry

1- Oxygen-containing functional groups- hydrophilicy

2- Aromatic carbon- Degree of Hidrophobocity

Activated Carbon Structure

Activated Carbon has a high surface area and relatively high porosity



Moreover, AC contains various heteroatoms such O, N, P, S and H.
However, the covalently bound atomic or adsorbed molecular oxygen is the major heteroatom, which can strongly alter the chemical properties of AC.

Schematic of the pore structure observed in AC

Biomass sources → -lignocellulosic biomass and crop waste residues from various agricultural and forestry processes.

Wood chips, coconut shell, sunflower seed hull and sugar cane bagasse, cocoa shells, pistachio shells, cotton stalks, corn shells, pine corns, corn cobs, barley husks, wood sawdust, orange peels..etc.

Wood chips

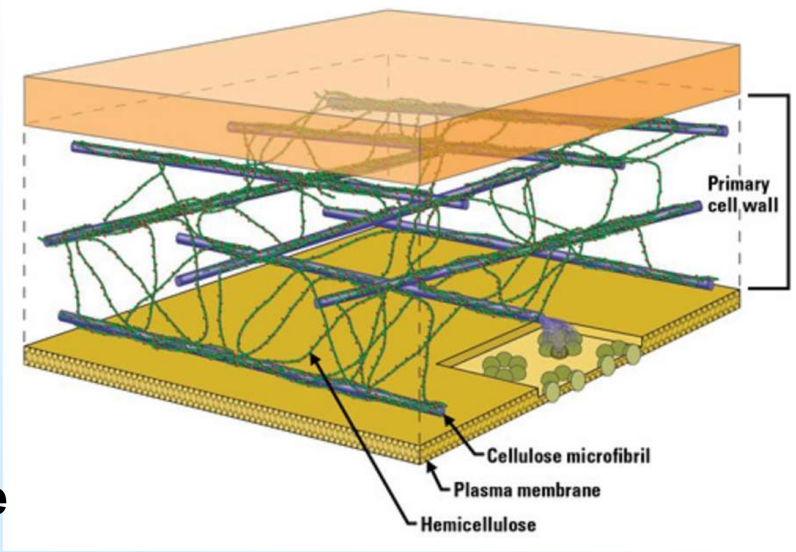
Coconut shell

Cocoa shell

Sugarcane bagasse

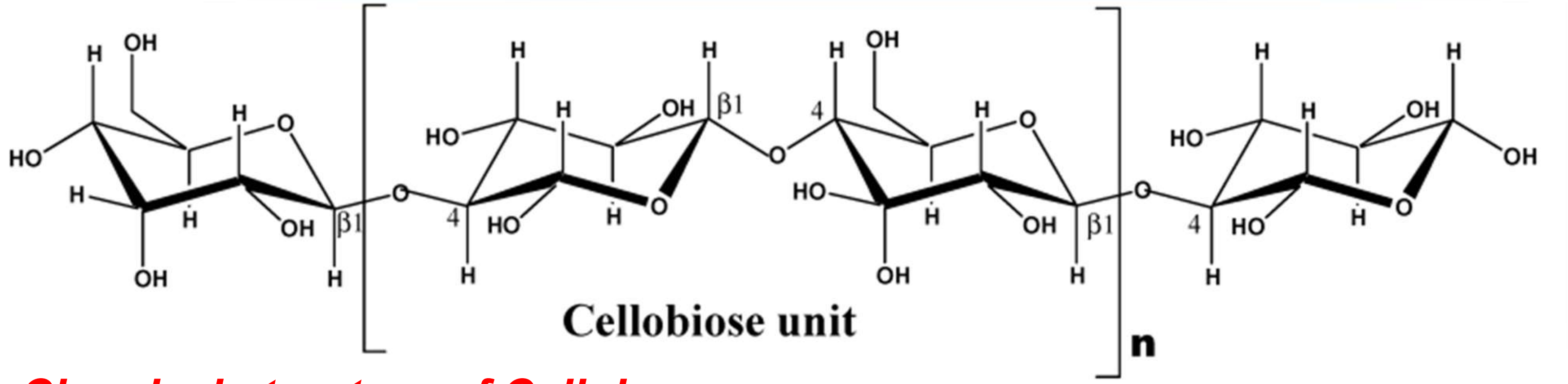
Lignocellulosic biomass

A 3-D polymeric composite,
Naturally recalcitrant to biological degradation
Polymeric constituents:



Lignocellulose structure.

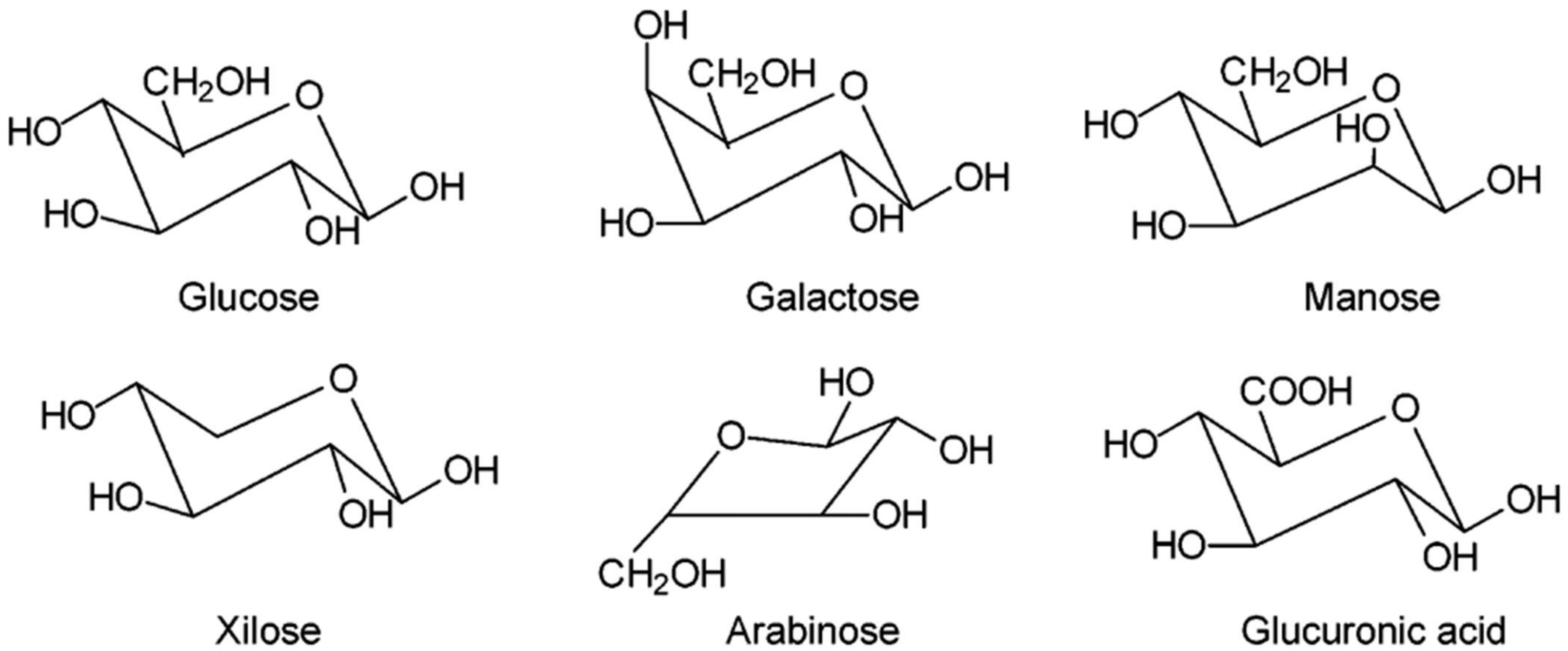
- Cellulose (40–60%w): linear chain of glucose linked by β-glycosidic linkage.



Chemical structure of Cellulose.

Lignocellulosic biomass

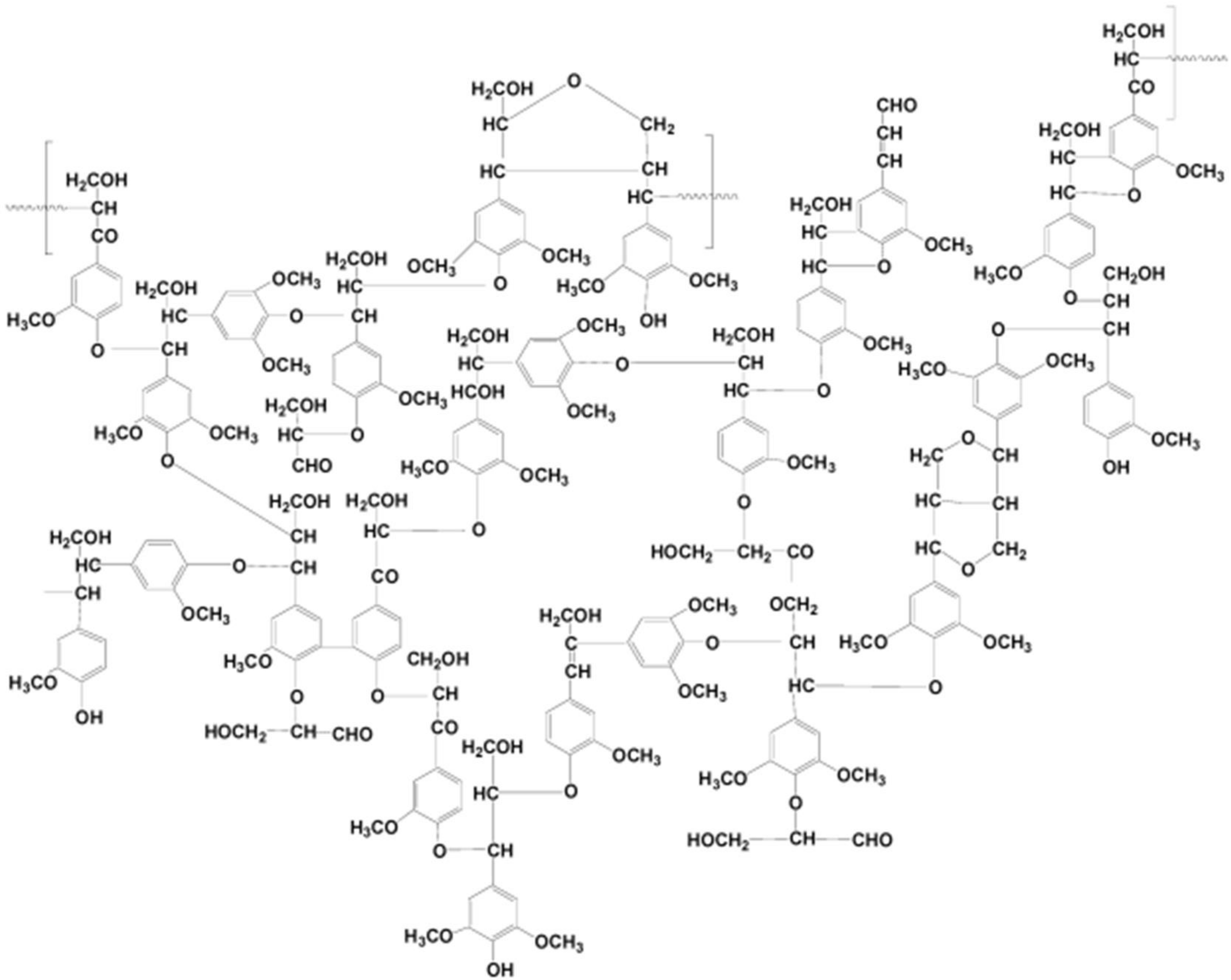
- **Hemicellulose (20–40%w): Sugars (C5 sugars such as D-xylose and L-arabinose, and C6 sugars such as D-galactose, D-glucose, and D-mannose) and uronic acid.**



Main components of hemicellulose

Lignocellulosic biomass

- **Lignin (10–25%w): A biopolymer rich in three-dimensional, highly branched polyphenolic constituents.**



Partial structure of a hardwood lignin molecule

Production of Activated Carbon

Two steps: carbonization and activation

Carbonization: carried out under inert atmosphere (pyrolysis) → termal decomposition of carbon source forming a carbonaceous material with no structure of pores

Activation: increase the pore diameter and generate other pores in the carbono material

ACTIVATION

Physical (thermical)

Chemical

Carbonization: Thermal treatment under N_2 (450°-600°C)

Activation: termal treatment at 800°-1100°C under $CO_2 + H_2O$; CO_2, or air

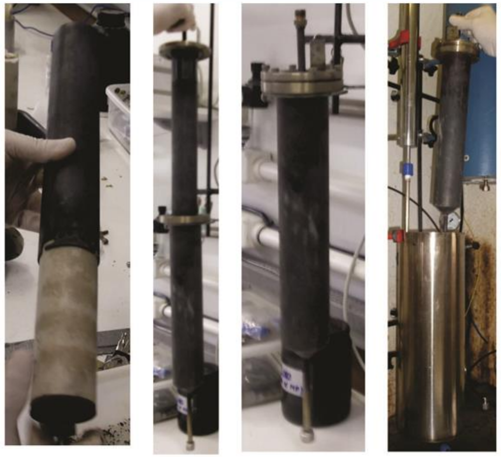
Single termal treatment (500°-750°C)

Carbon precursor is mixed with $ZnCl_2$, H_3PO_4, NaOH, $FeCl_3$, $CuCl_2$, etc

Leaching out of the inorganics

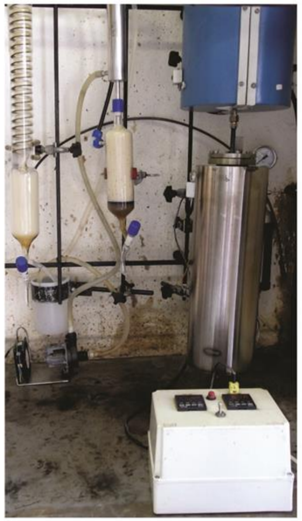
Cylinder for preparation of activated carbon

Carbon material cylinder dried

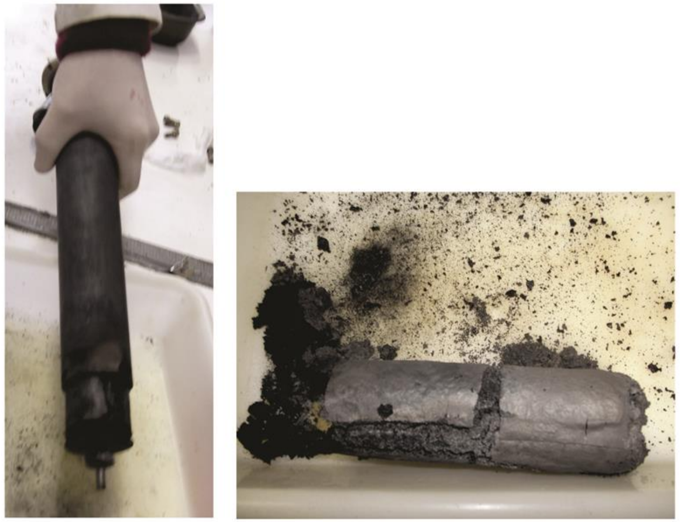


Cylinder introduced into reactor

Furnace setup



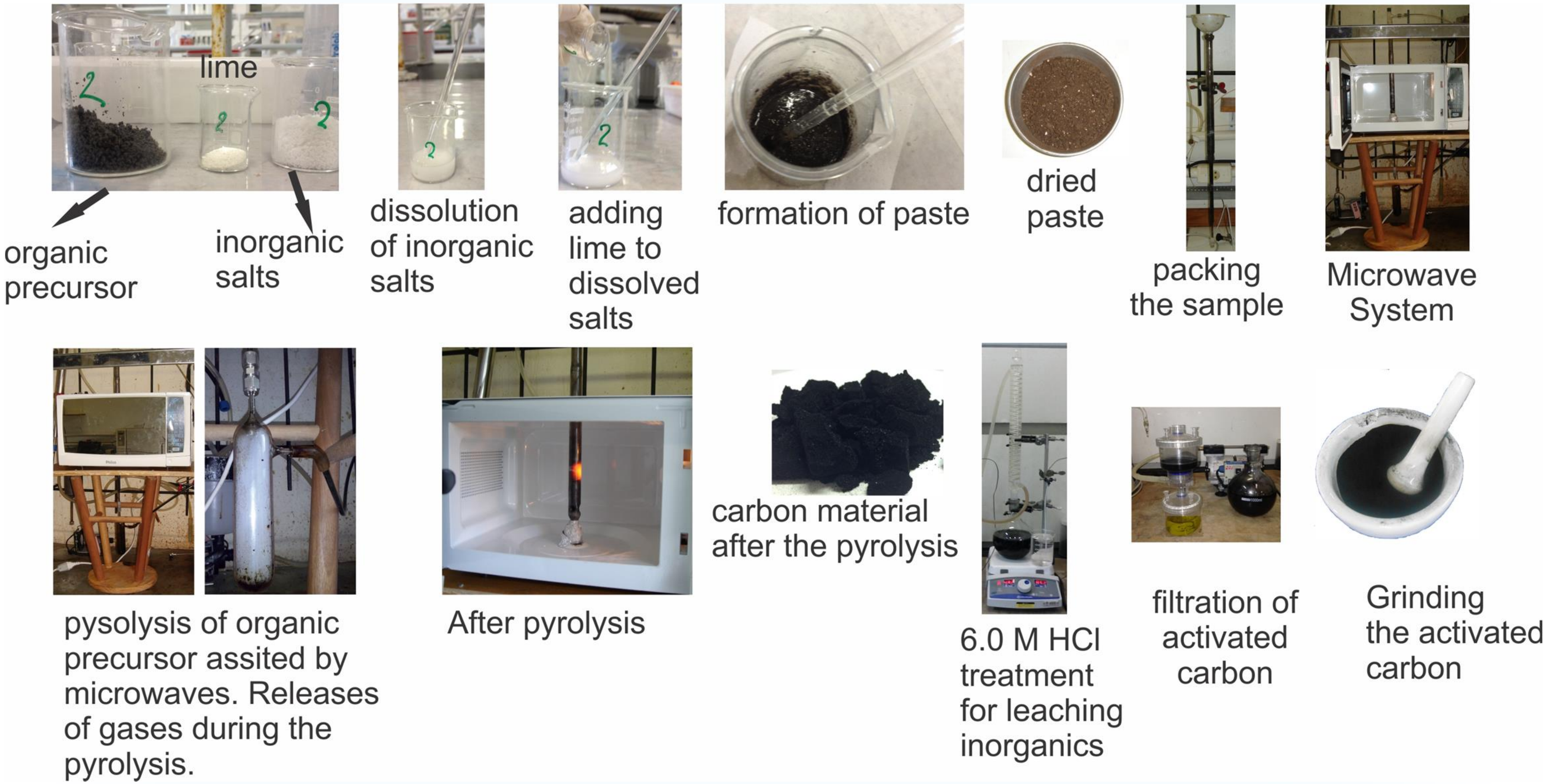
Oil extracted from biomass

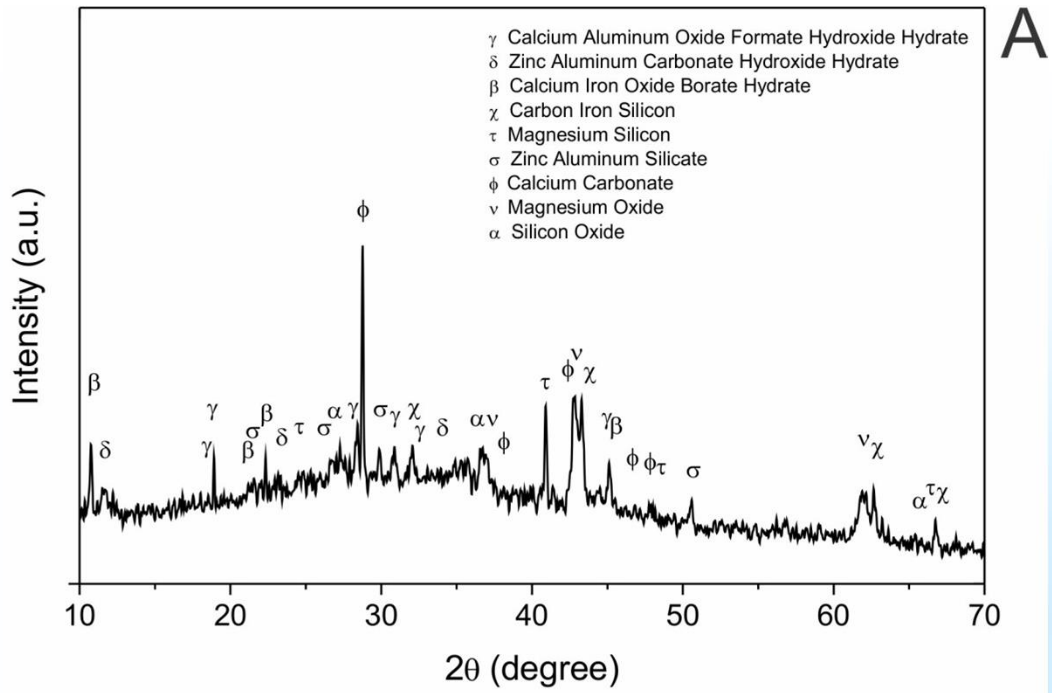


carbon material removed in cylinder form out of reactor

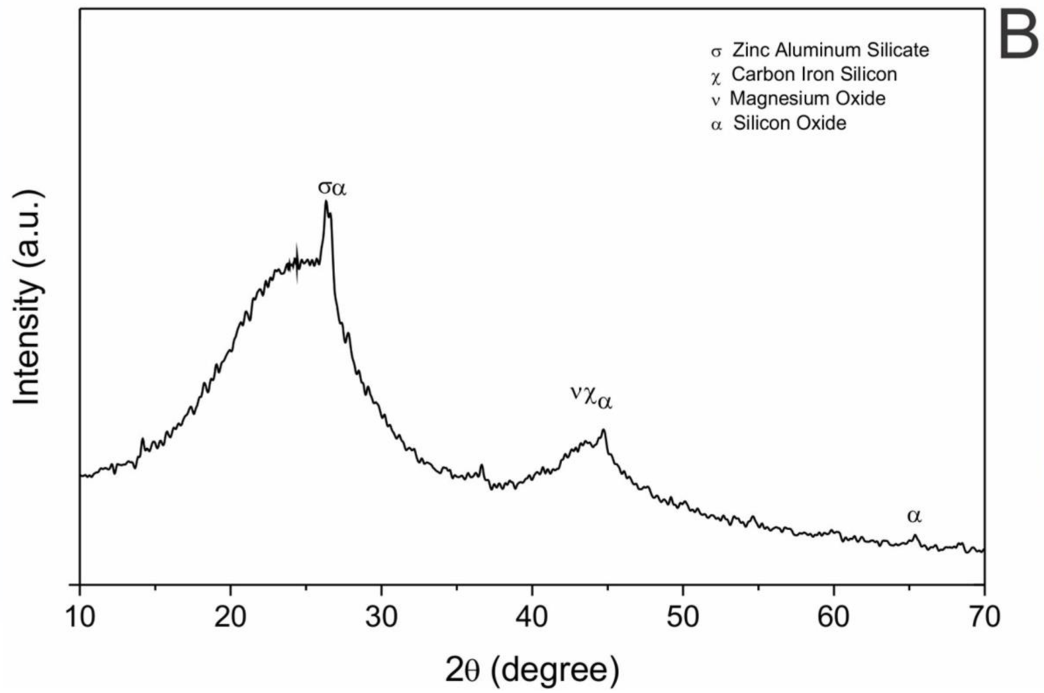
Activation step: Lixiviation of inorganics and filtration

Activated Carbon

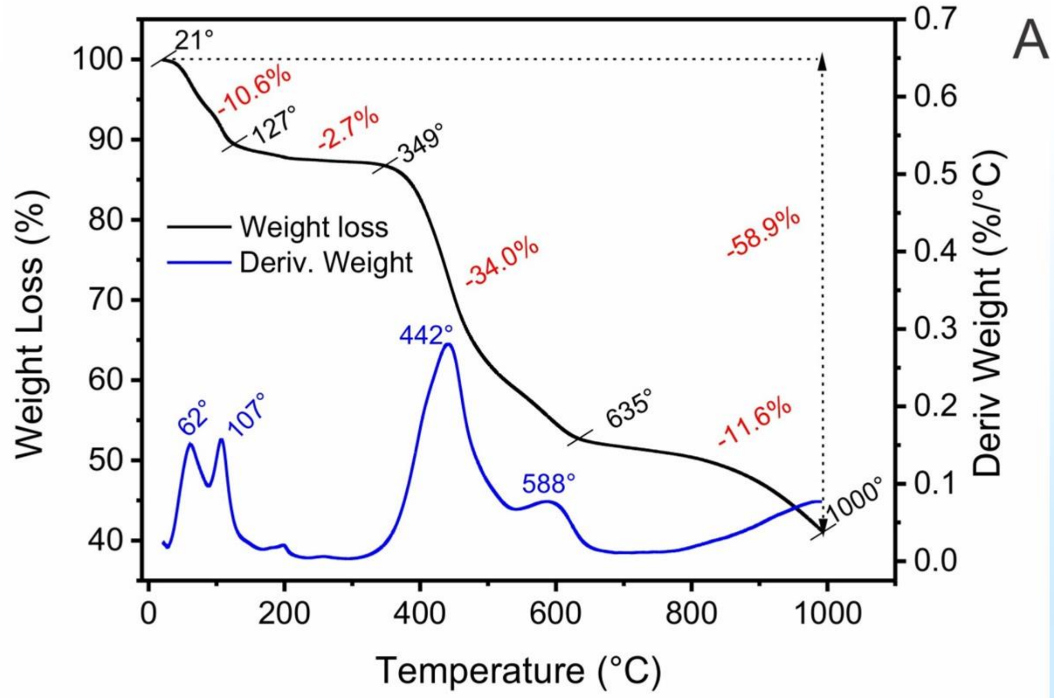

lime
organic precursor
inorganic salts
dissolution of inorganic salts
adding lime to dissolved salts
formation of paste
dried paste
packing the sample
Microwave System
pysolysis of organic precursor assited by microwaves. Releases of gases during the pyrolysis.
After pyrolysis
carbon material after the pyrolysis
6.0 M HCl treatment for leaching inorganics
filtration of activated carbon
Grinding the activated carbon



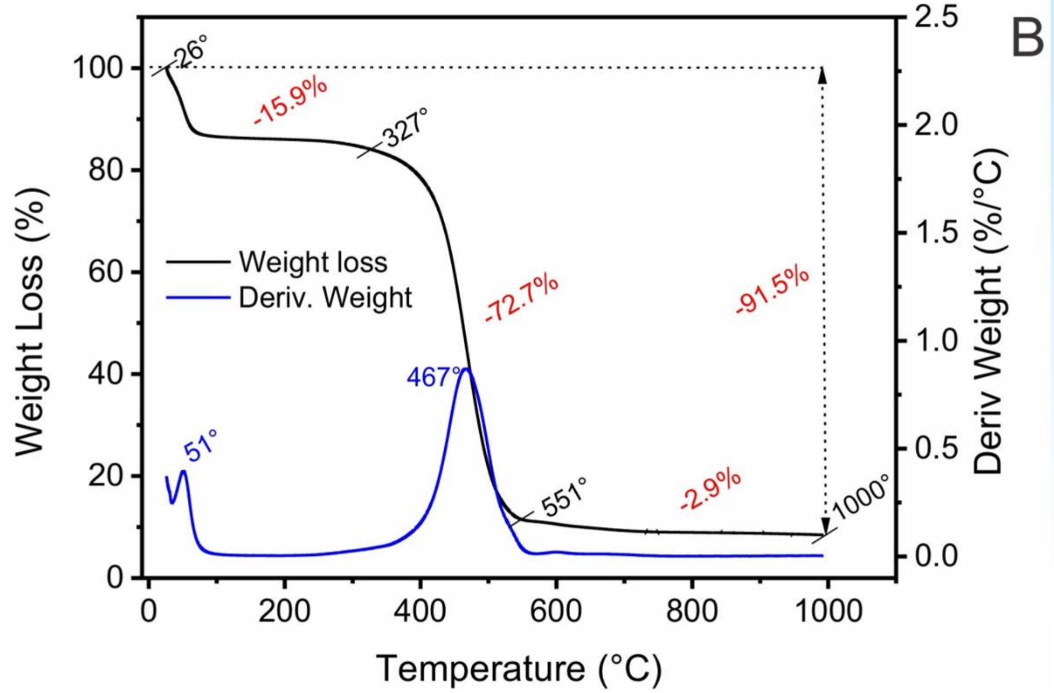
Before leaching out of inorganics



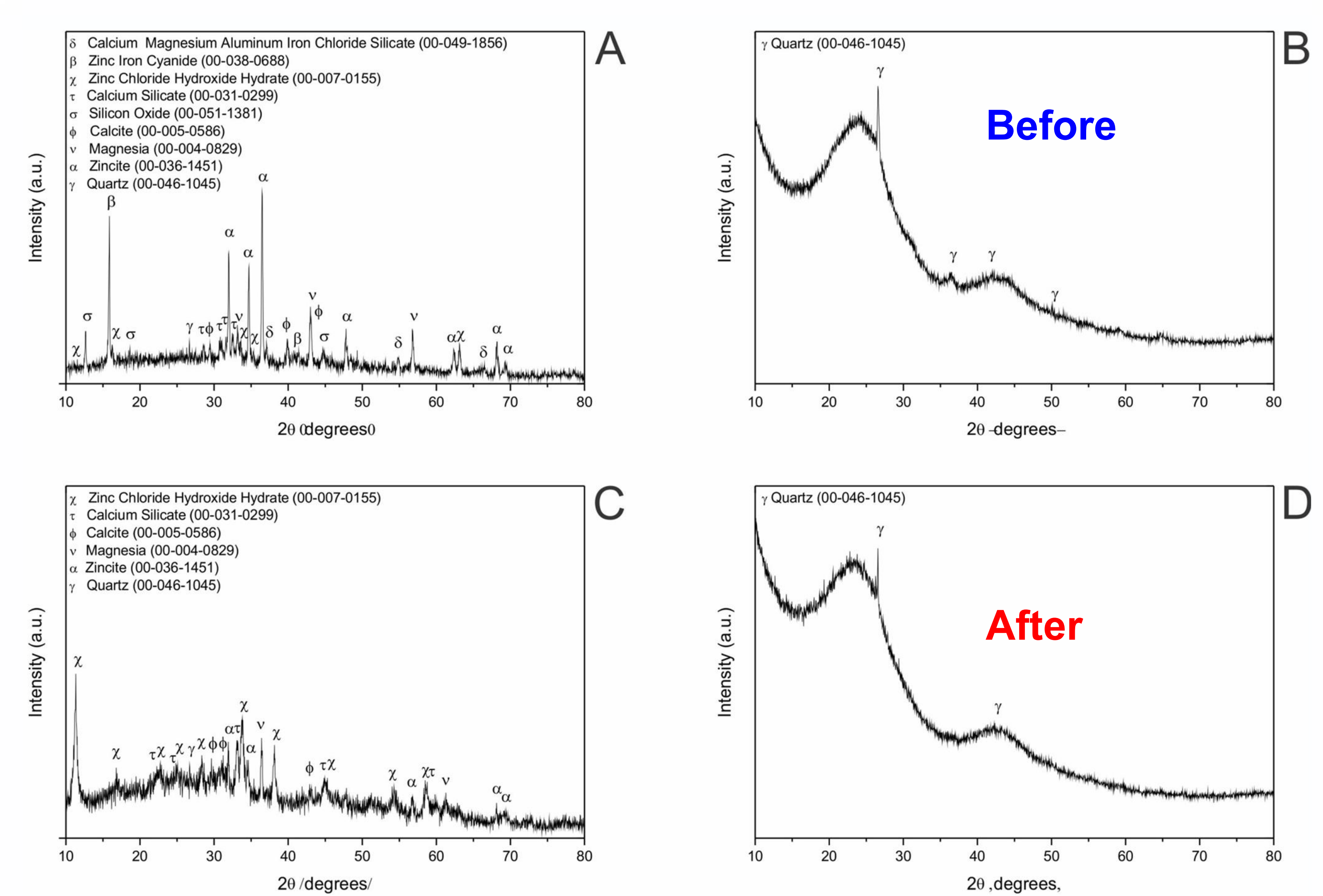
After leaching out of inorganics

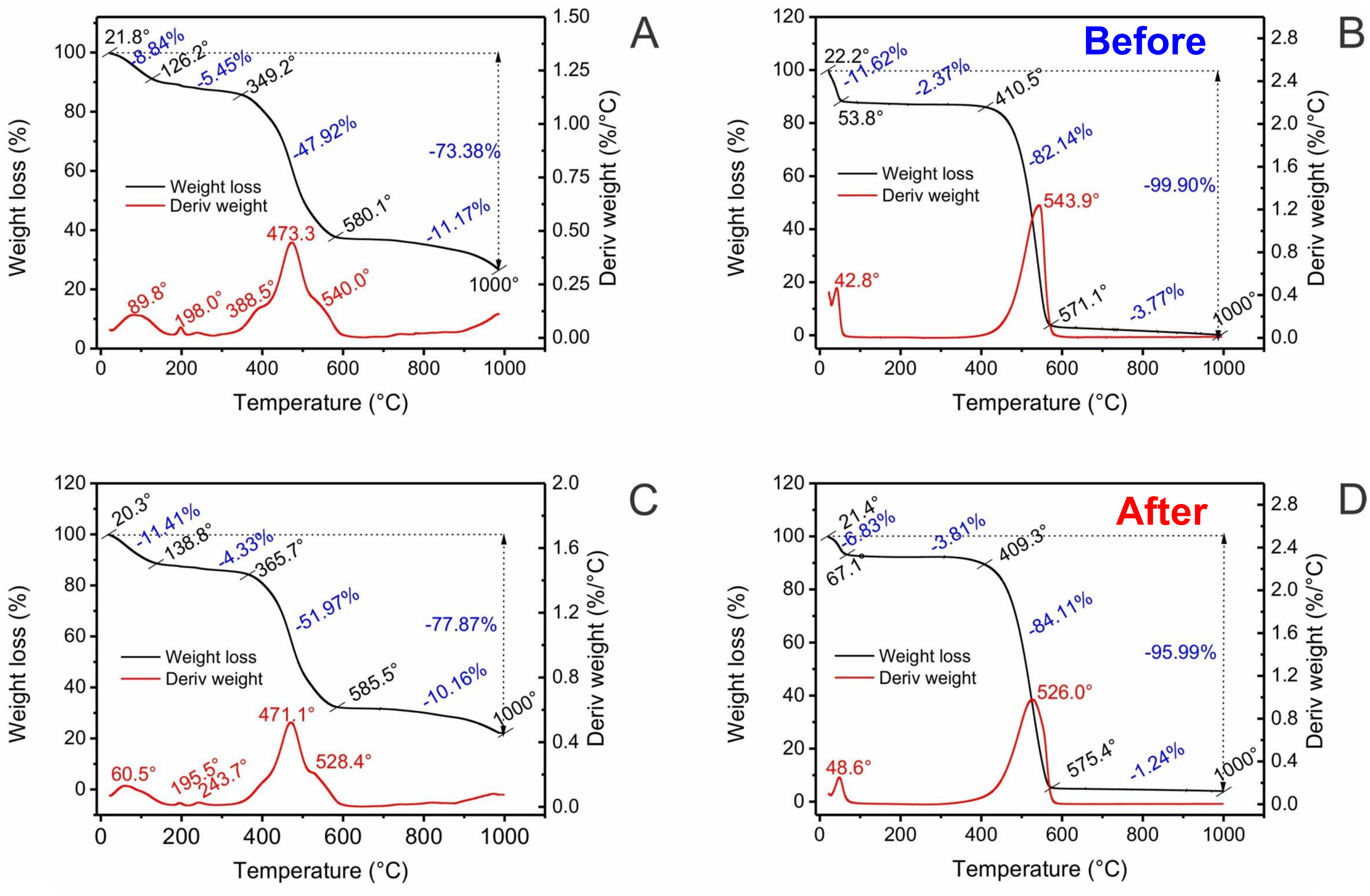


Before leaching out of inorganics

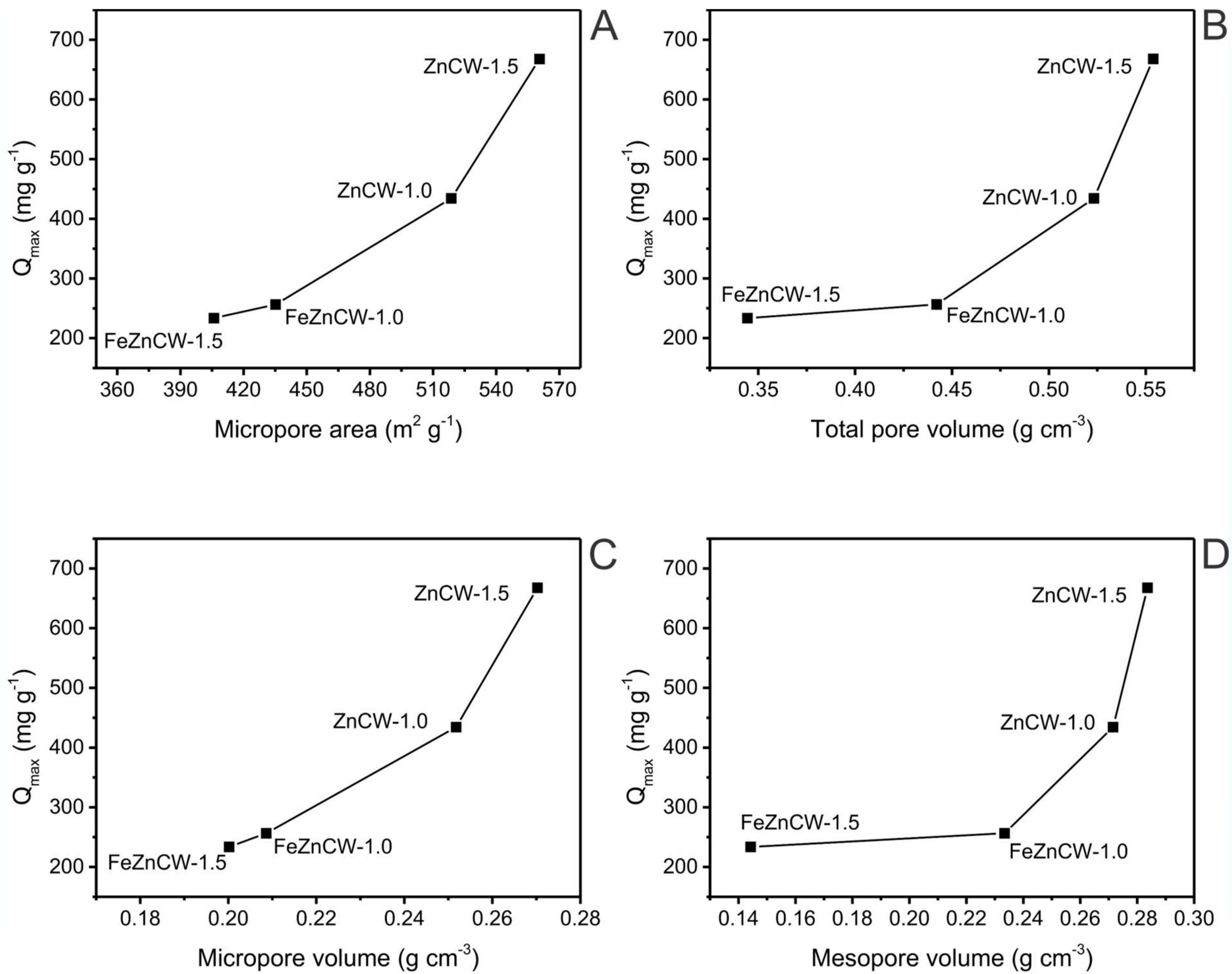


After leaching out of inorganics


A
δ Calcium Magnesium Aluminum Iron Chloride Silicate (00-049-1856)
β Zinc Iron Cyanide (00-038-0688)
χ Zinc Chloride Hydroxide Hydrate (00-007-0155)
τ Calcium Silicate (00-031-0299)
σ Silicon Oxide (00-051-1381)
ϕ Calcite (00-005-0586)
ν Magnesia (00-004-0829)
α Zincite (00-036-1451)
γ Quartz (00-046-1045)
Intensity (a.u.)
2θ (degrees)
B
γ Quartz (00-046-1045)
Before
Intensity (a.u.)
2θ (degrees)
C
χ Zinc Chloride Hydroxide Hydrate (00-007-0155)
τ Calcium Silicate (00-031-0299)
ϕ Calcite (00-005-0586)
ν Magnesia (00-004-0829)
α Zincite (00-036-1451)
γ Quartz (00-046-1045)
Intensity (a.u.)
2θ (degrees)
D
γ Quartz (00-046-1045)
After
Intensity (a.u.)
2θ (degrees)



A
Weight loss
Deriv weight
21.8°
-8.84%
126.2°
-5.45%
349.2°
-47.92%
-73.38%
580.1°
-11.17%
1000°
473.3
89.8°
198.0°
388.5°
540.0°
Weight loss (%)
Deriv weight (%/°C)
Temperature (°C)
B
Before
22.2°
-11.62%
-2.37%
410.5°
53.8°
-82.14%
-99.90%
543.9°
42.8°
571.1°
-3.77%
1000°
C
20.3°
-11.41%
138.8°
-4.33%
365.7°
-51.97%
-77.87%
585.5°
-10.16%
1000°
471.1°
60.5°
195.5°
243.7°
528.4°
D
After
21.4°
-6.83%
-3.81%
409.3°
67.1°
-84.11%
-95.99%
526.0°
48.6°
575.4°
-1.24%
1000°


A
B
C
D
ZnCW-1.5
ZnCW-1.0
FeZnCW-1.0
FeZnCW-1.5
Q_max (mg g^-1)
Micropore area (m^2 g^-1)
Total pore volume (g cm^-3)
Micropore volume (g cm^-3)
Mesopore volume (g cm^-3)

Design of Experiments for exploring pyrolysis temperature and holding time of avocado seed (AS)

Experiment	Samples	T_f (°C)	Hold time (min)
1	ASAC1	500	30
2	ASAC2	700	30
3	ASAC3	500	60
4	ASAC4	700	60
5	ASAC5	600	45
6	ASAC6	600	45
7	ASAC7	600	45

		levels	
	-1	0	1
T_f (°C)	500	600	700
Hold time (min)	30	45	60

Textural properties of avocado seed activated carbons.

Sample	BET surface area ($m^2\ g^{-1}$)	t-Plot Micropore Area ($m^2\ g^{-1}$)	t-plot extern. surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	t-Plot micropore volume ($cm^3\ g^{-1}$)	Mesopore volume ($cm^3\ g^{-1}$)
ASAC1	1584	360	1224	0.8469	0.1563	0.6906
ASAC2	1230	201	1029	0.6685	0.0838	0.5847
ASAC3	1370	263	1107	0.7664	0.1120	0.6544
ASAC4	1122	284	838	0.6002	0.1249	0.4753
ASAC5	1343	316	1027	0.7354	0.1354	0.6000
ASAC6	1300	250	1050	0.7248	0.1261	0.5987
ASAC7	1310	237	1073	0.7232	0.1376	0.5856

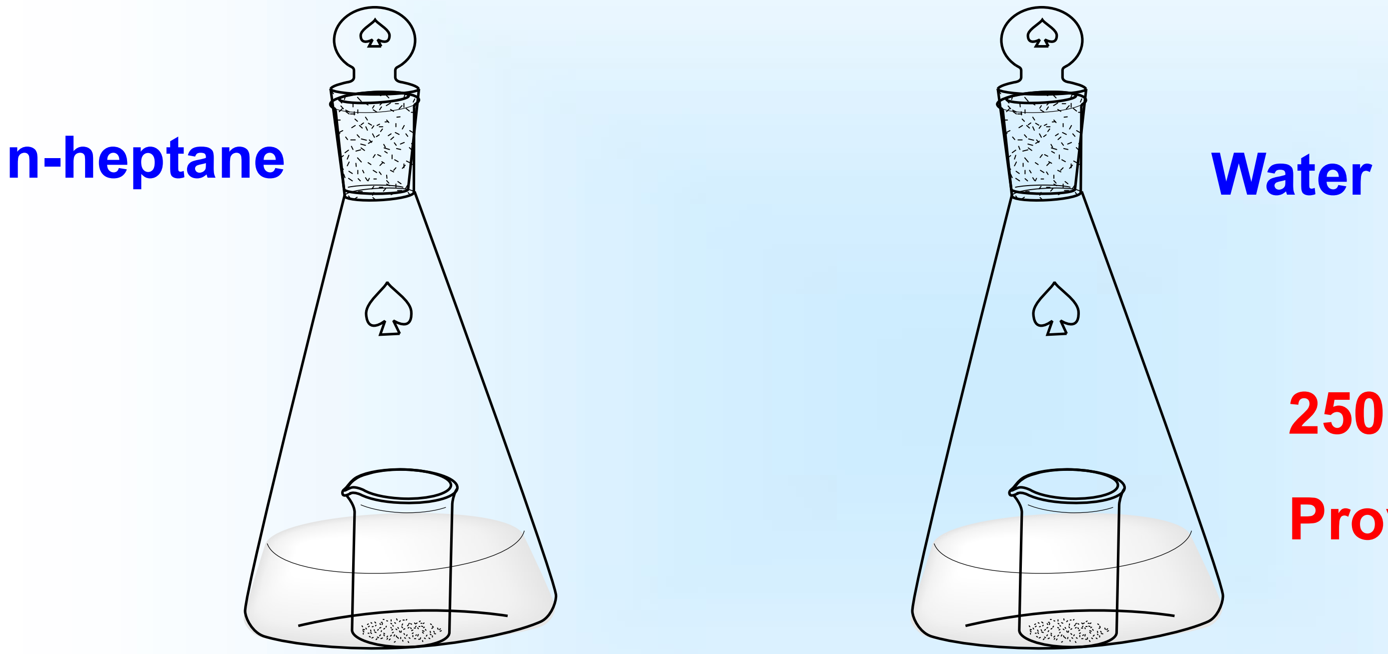
Samples	T_f (°C)	Hold time (min)
ASAC1	500	30
ASAC2	700	30
ASAC3	500	60
ASAC4	700	60
ASAC5	600	45
ASAC6	600	45
ASAC7	600	45

Chemical surface properties of avocado seed activated carbons.

Sample	pH_{pzc}	Total acidity (mmol g^{-1})	Total basicity (mmol g^{-1})	Total of functional groups (mmol g^{-1})	HI
ASAC1	6.11	0.2950	0.1885	0.4835	0.7884
ASAC2	6.80	0.2054	0.1568	0.3622	0.8750
ASAC3	6.32	0.2831	0.1475	0.4306	0.7889
ASAC4	6.85	0.1907	0.1590	0.3497	0.9146
ASAC5	6.48	0.2145	0.1547	0.3692	0.8047
ASAC6	6.55	0.2245	0.1547	0.3792	0.8045
ASAC7	6.52	0.2137	0.1608	0.3745	0.8041

Samples	T_f (°C)	Hold time (min)
ASAC1	500	30
ASAC2	700	30
ASAC3	500	60
ASAC4	700	60
ASAC5	600	45
ASAC6	600	45
ASAC7	600	45

$$HI = \frac{mass\ of\ \ n\text{-}heptane\ adsorbed/m\ AC}{mass\ of\ \ water\ adsorbed/m\ AC}$$



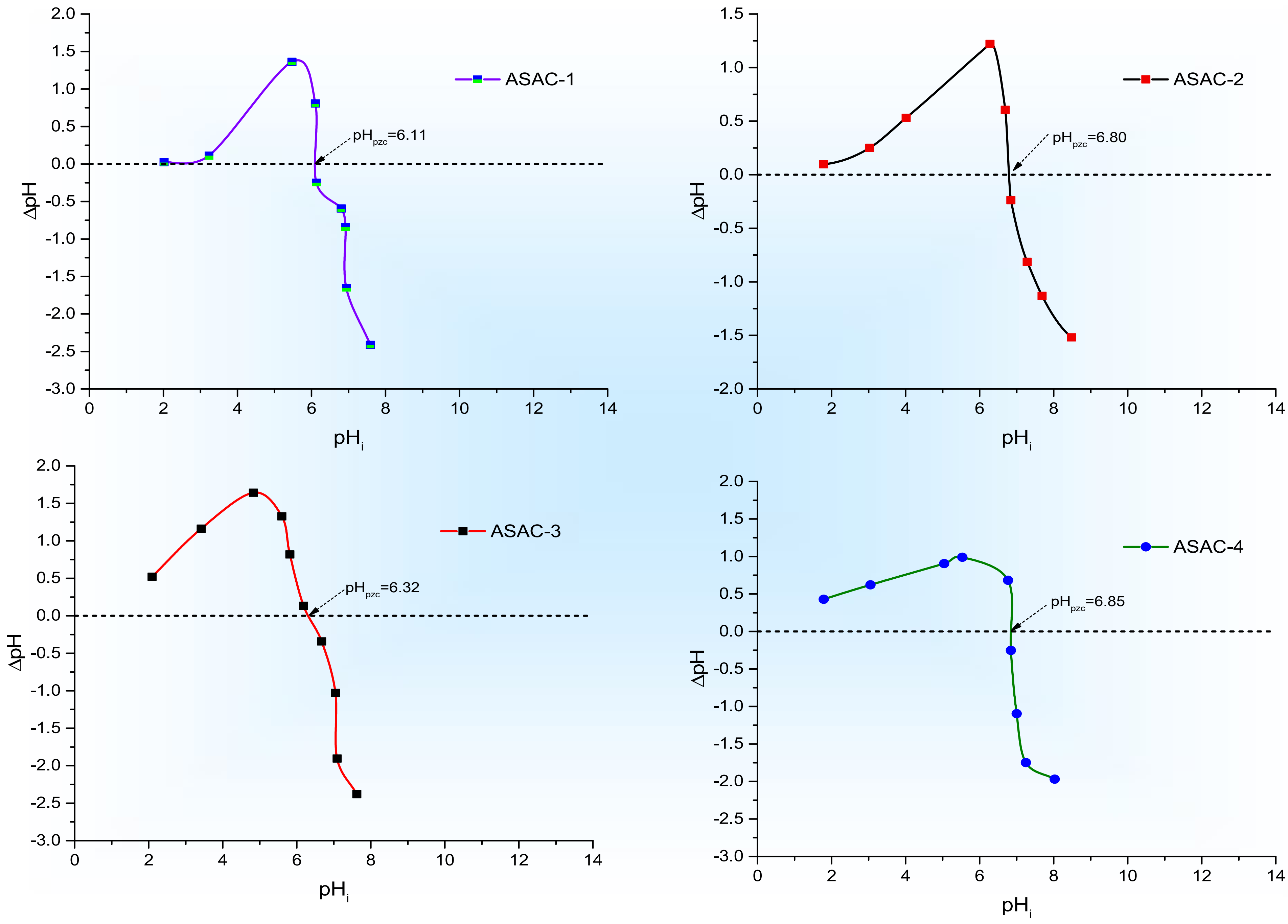
250 mL Erlenmeyer

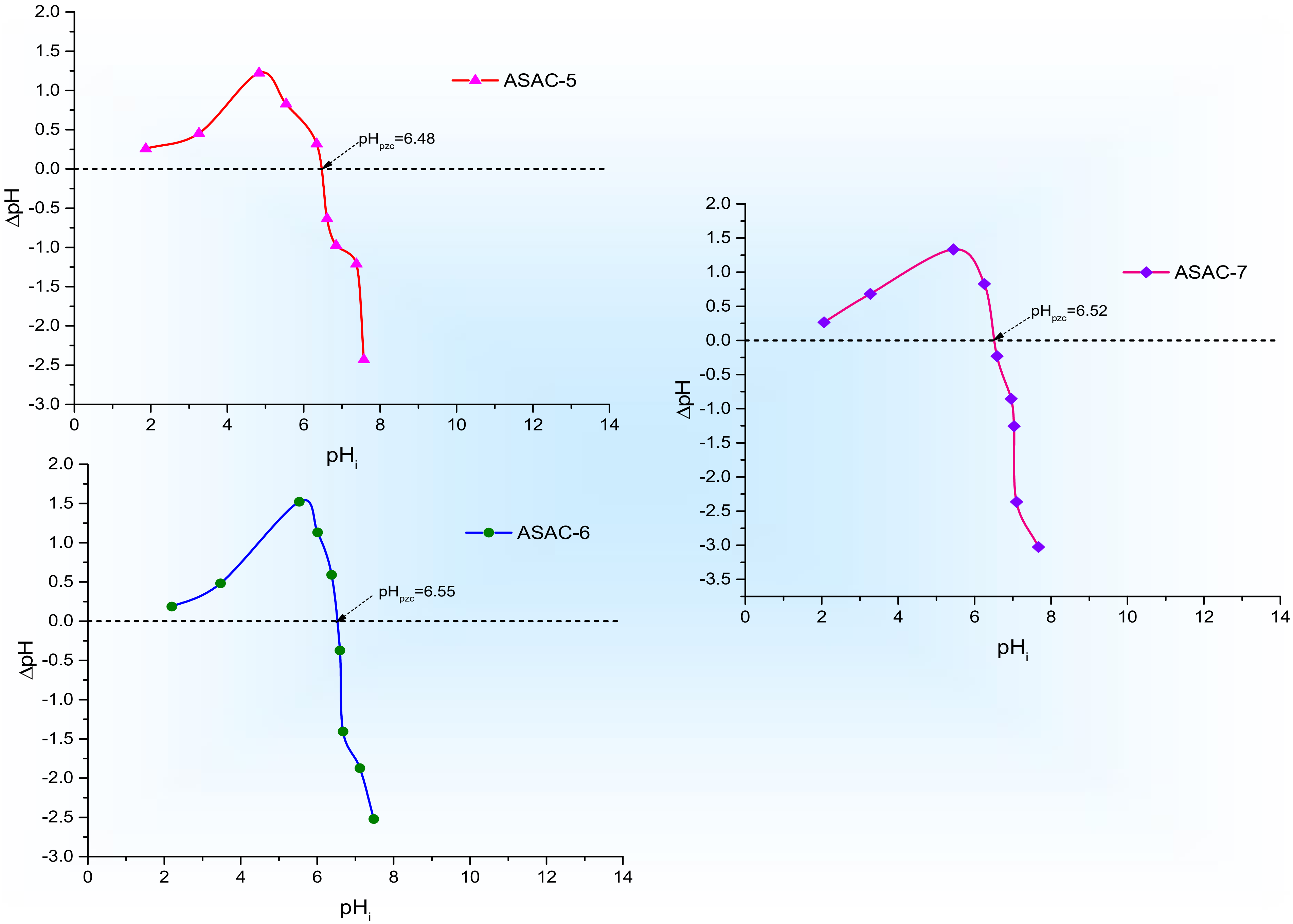
Provided with glass joint

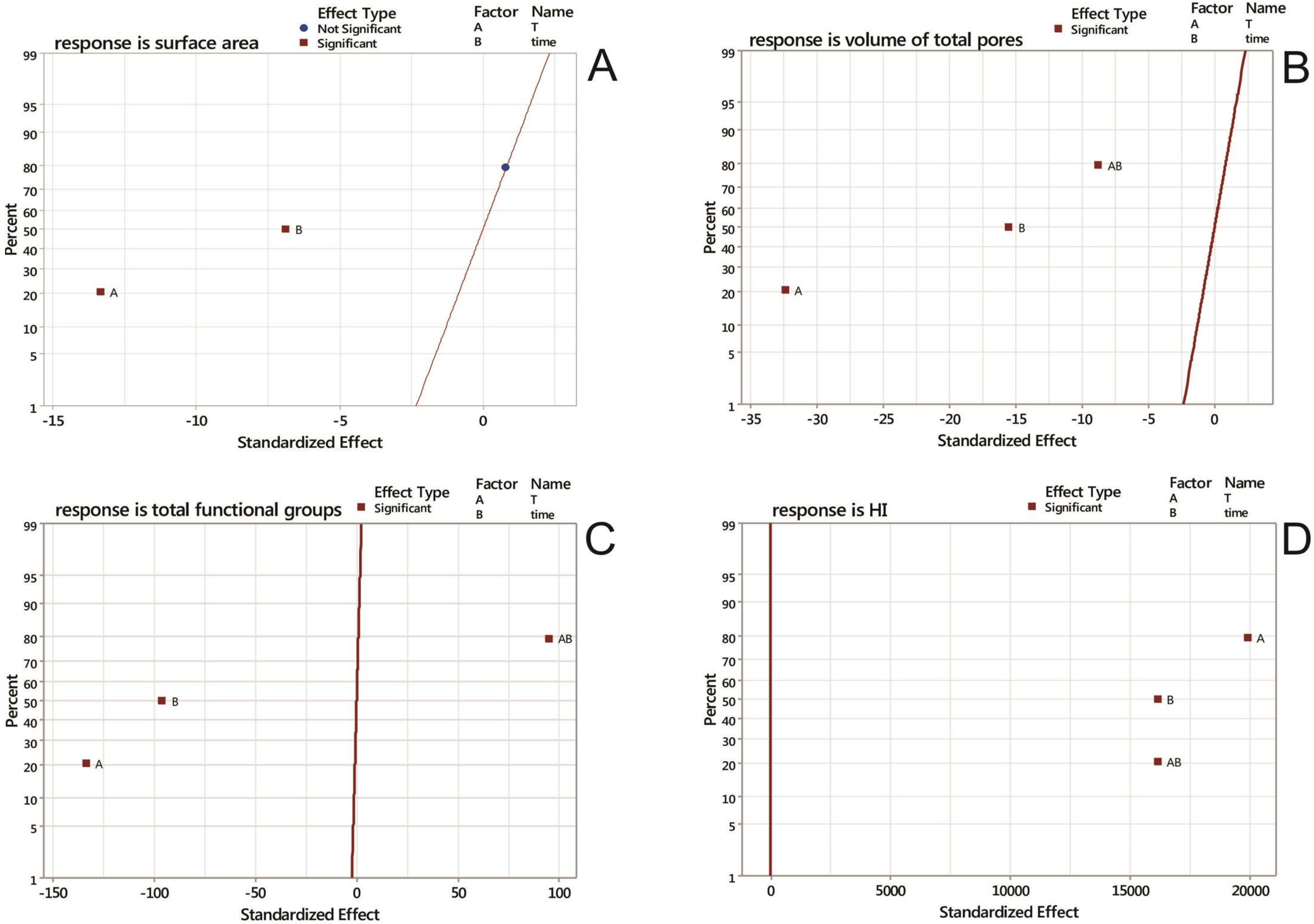
300 mg solid sample inside the 10 mL Becker

60 mL solvent

T= 25°C, no stirring


ASAC-1
pH$_{pzc}$=6.11
ΔpH
pH$_i$
ASAC-2
pH$_{pzc}$=6.80
ΔpH
pH$_i$
ASAC-3
pH$_{pzc}$=6.32
ΔpH
pH$_i$
ASAC-4
pH$_{pzc}$=6.85
ΔpH
pH$_i$


ASAC-5
pH$_{pzc}$=6.48
ΔpH
pH$_{i}$
ASAC-6
pH$_{pzc}$=6.55
ASAC-7
pH$_{pzc}$=6.52


A
response is surface area
Effect Type
Not Significant
Significant
Factor Name
A T
B time
Percent
Standardized Effect
B
response is volume of total pores
Effect Type
Significant
Factor Name
A T
B time
Percent
Standardized Effect
C
response is total functional groups
Effect Type
Significant
Factor Name
A T
B time
Percent
Standardized Effect
D
response is HI
Effect Type
Significant
Factor Name
A T
B time
Percent
Standardized Effect

Factorial Regression: S_{BET} versus T; time; Center Point

Term	Coefficient	Standard Error of Coeff	Probability	Contribution (%)
Constant	$-7.66.10^{-4}$	6.10^{-6}	0.000	
T	$-8.6.10^{-5}$	6.10^{-6}	0.006	77.90
time	$-4.4.10^{-5}$	6.10^{-6}	0.021	20.71
Txtime	5.10^{-6}	6.10^{-6}	0.512	0.27
Center point	7.10^{-6}	$1.0.10^{-5}$	0.534	0.24
Error				0.88

A

R^2 0.9912; R^2_{adj} 0.9737

Factorial Regression: Total volume of pores versus T; time; Center Point

Term	Coefficient	Standard Error of Coeff	Probability	Contribution (%)
Constant	-0.15618	0.00307	0.000	
T	-0.09934	0.00307	0.001	71.28
time	-0.04765	0.00307	0.004	16.40
Txtime	-0.02692	0.00307	0.013	5.23
Center point	0.04741	0.00468	0.010	6.96
Error				0.13

B

R^2 0.9968; R^2_{adj} 0.9959

Factorial Regression: Total functional groups versus T; time; Center Poi.

Term	Coefficient	Standard Error of Coeff	Probability	Contribution (%)
Constant	-34874.9	0.00139	0.000	
T	-0.18577	0.00139	0.000	41.42
time	-0.13342	0.00139	0.000	21.37
Txtime	0.13169	0.00139	0.000	20.82
Center point	-0.17849	0.00212	0.000	16.39
Error				0.00

C

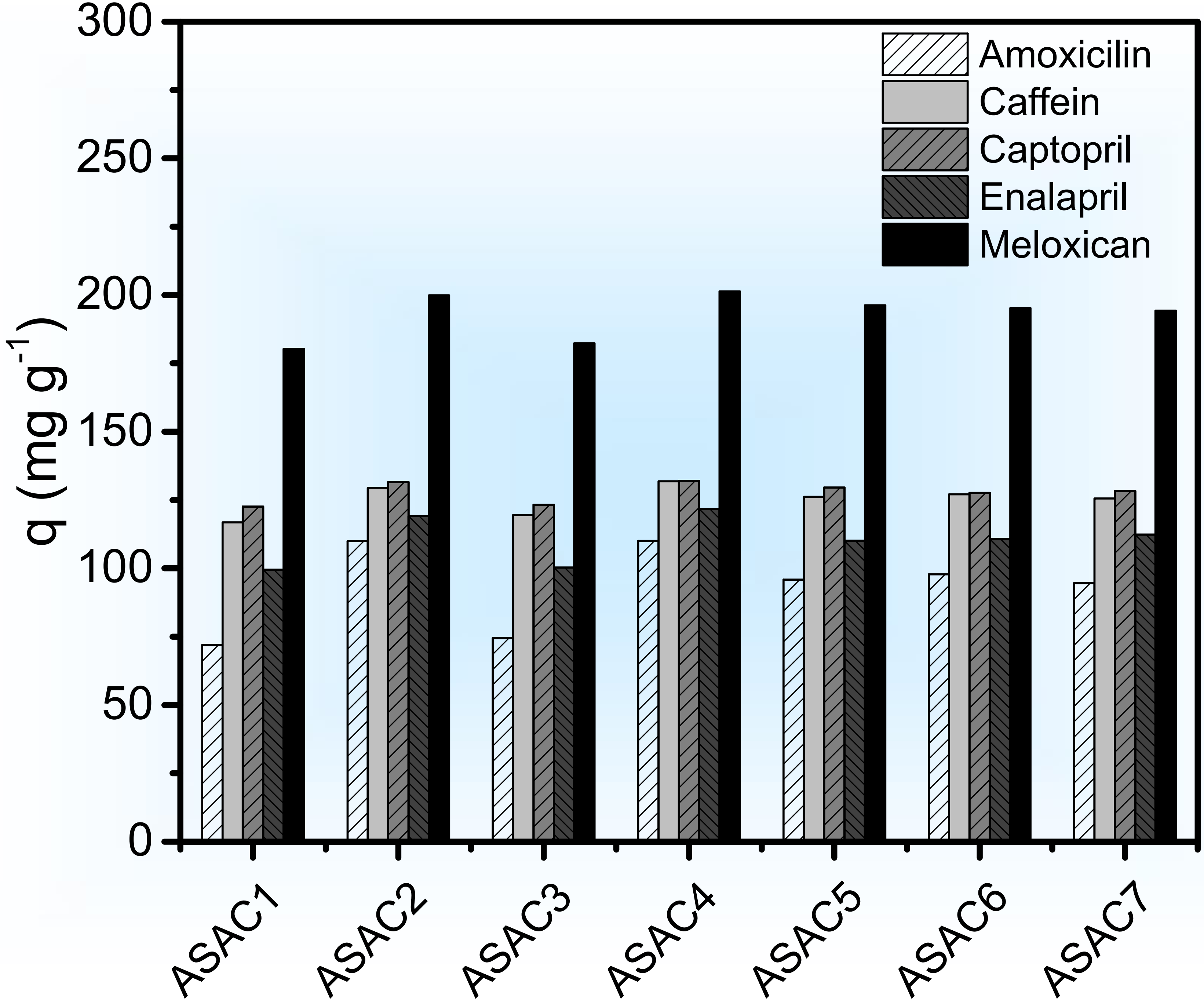
R^2 1.000; R^2_{adj} 0.9999

Factorial Regression: HI versus T; time; Center Point

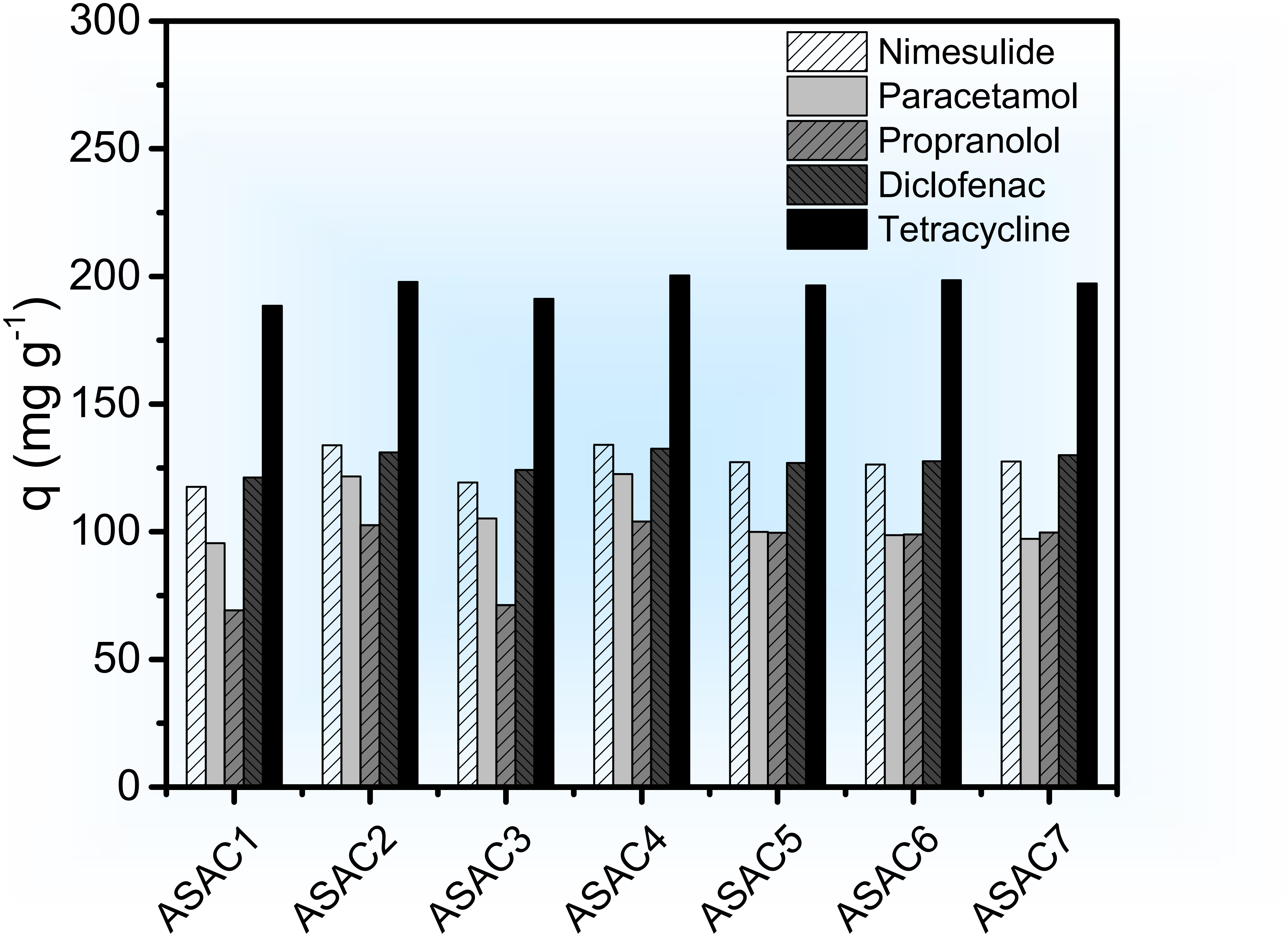
Term	Coefficient	Standard Error of Coeff	Probability	Contribution (%)
Constant	-302.417	0.000044	0.000	
T	0.881873	0.000044	0.000	36.47
time	0.715516	0.000044	0.000	24.01
Txtime	0.715489	0.000044	0.000	24.00
Center point	-0.878954	0.000068	0.000	15.52
Error				0.00

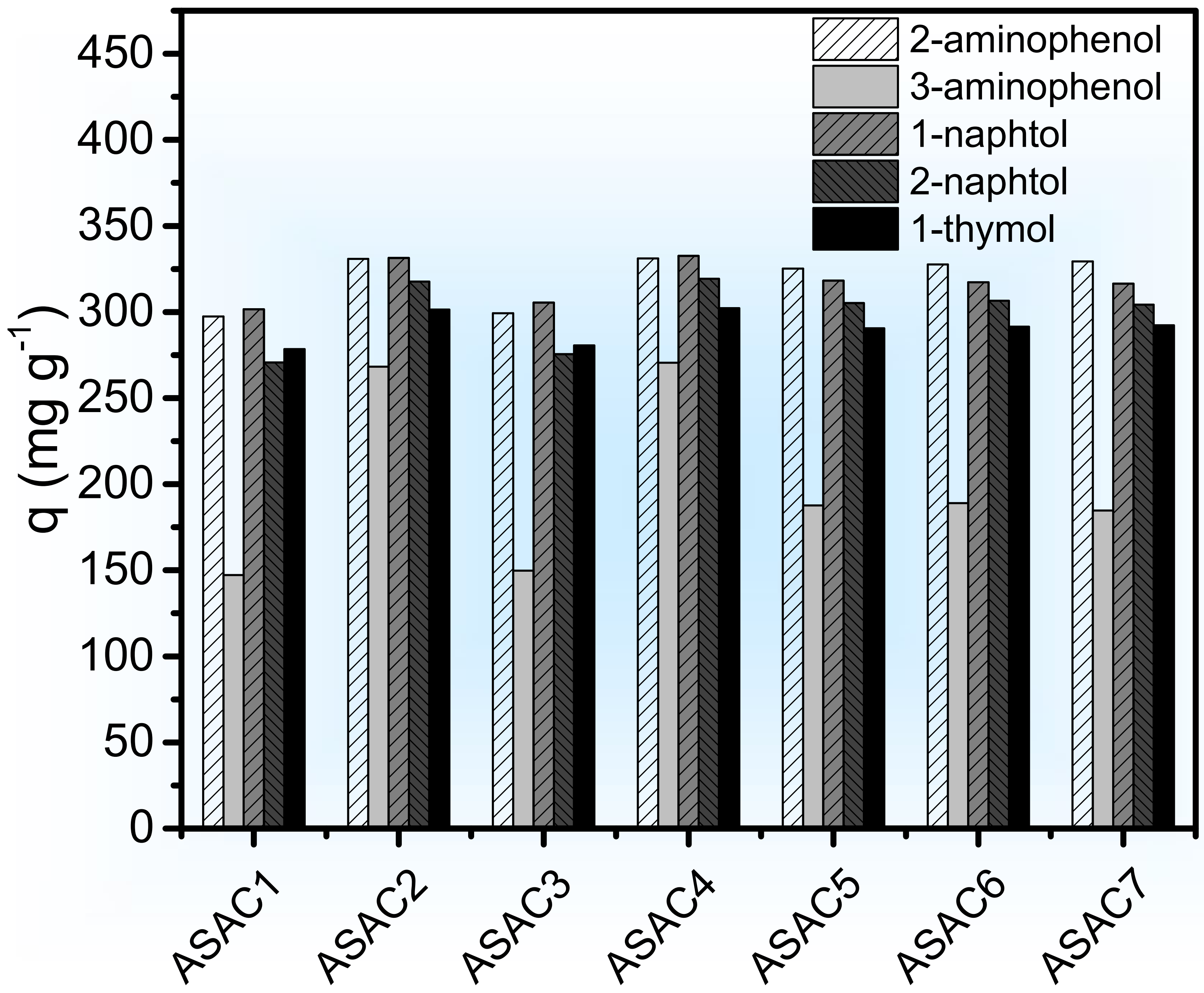
D

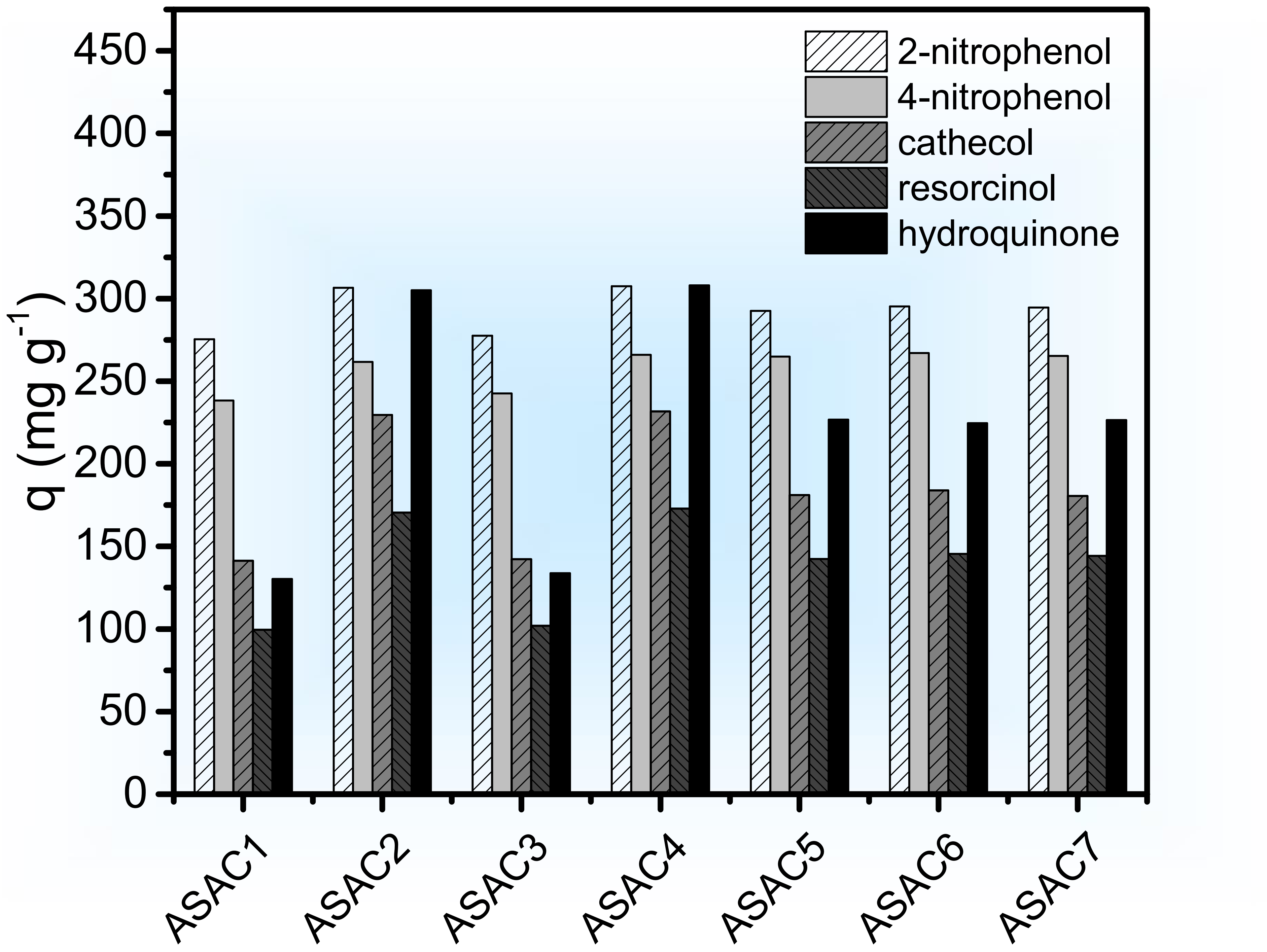
R^2 1.000; R^2_{adj} 1.000

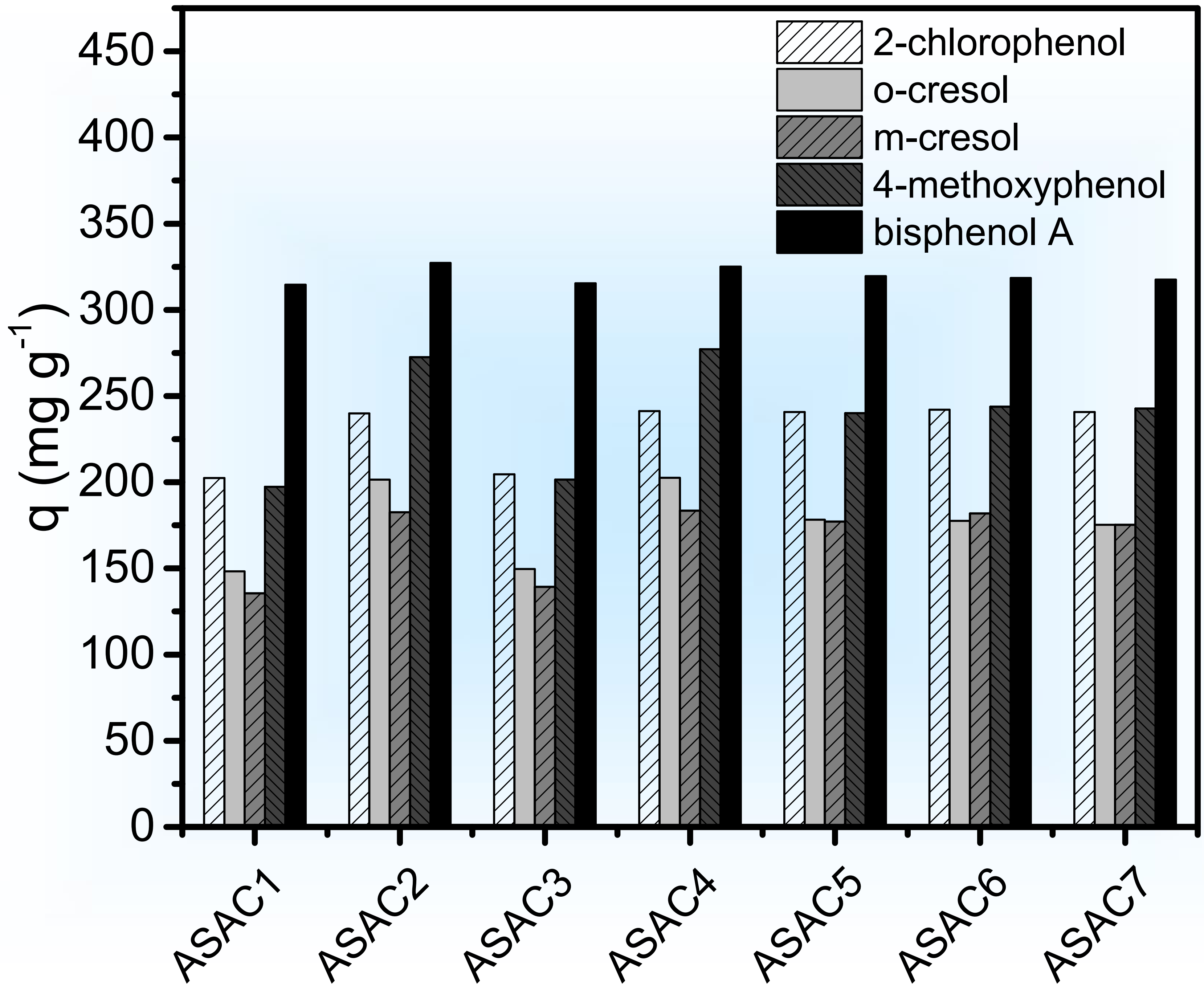


300
250
200
150
100
50
0
q (mg g^{-1})
Amoxicilin
Caffein
Captopril
Enalapril
Meloxican
ASAC1
ASAC2
ASAC3
ASAC4
ASAC5
ASAC6
ASAC7

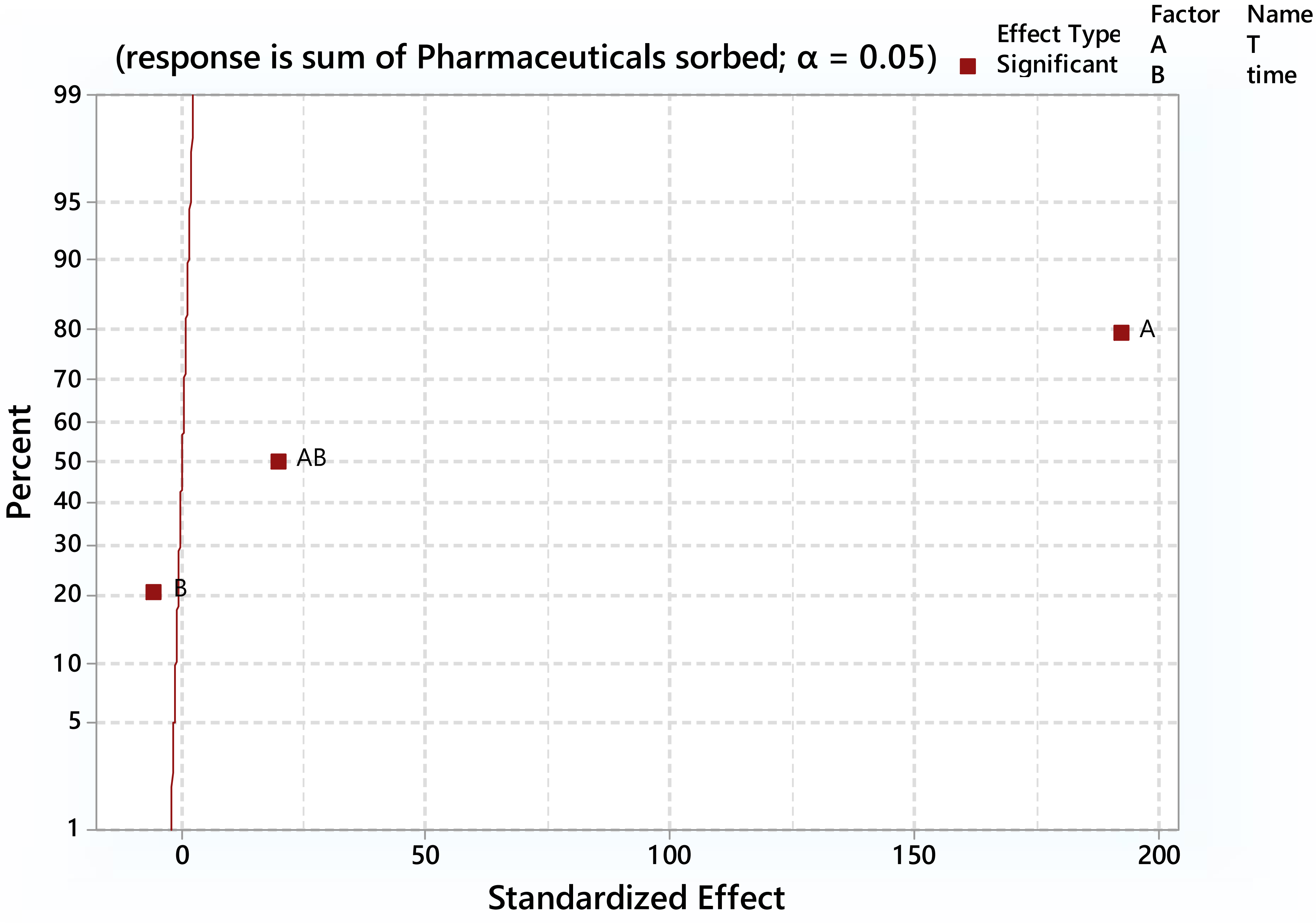

Nimesulide
Paracetamol
Propranolol
Diclofenac
Tetracycline
q (mg g-1)
300
250
200
150
100
50
0
ASAC1
ASAC2
ASAC3
ASAC4
ASAC5
ASAC6
ASAC7

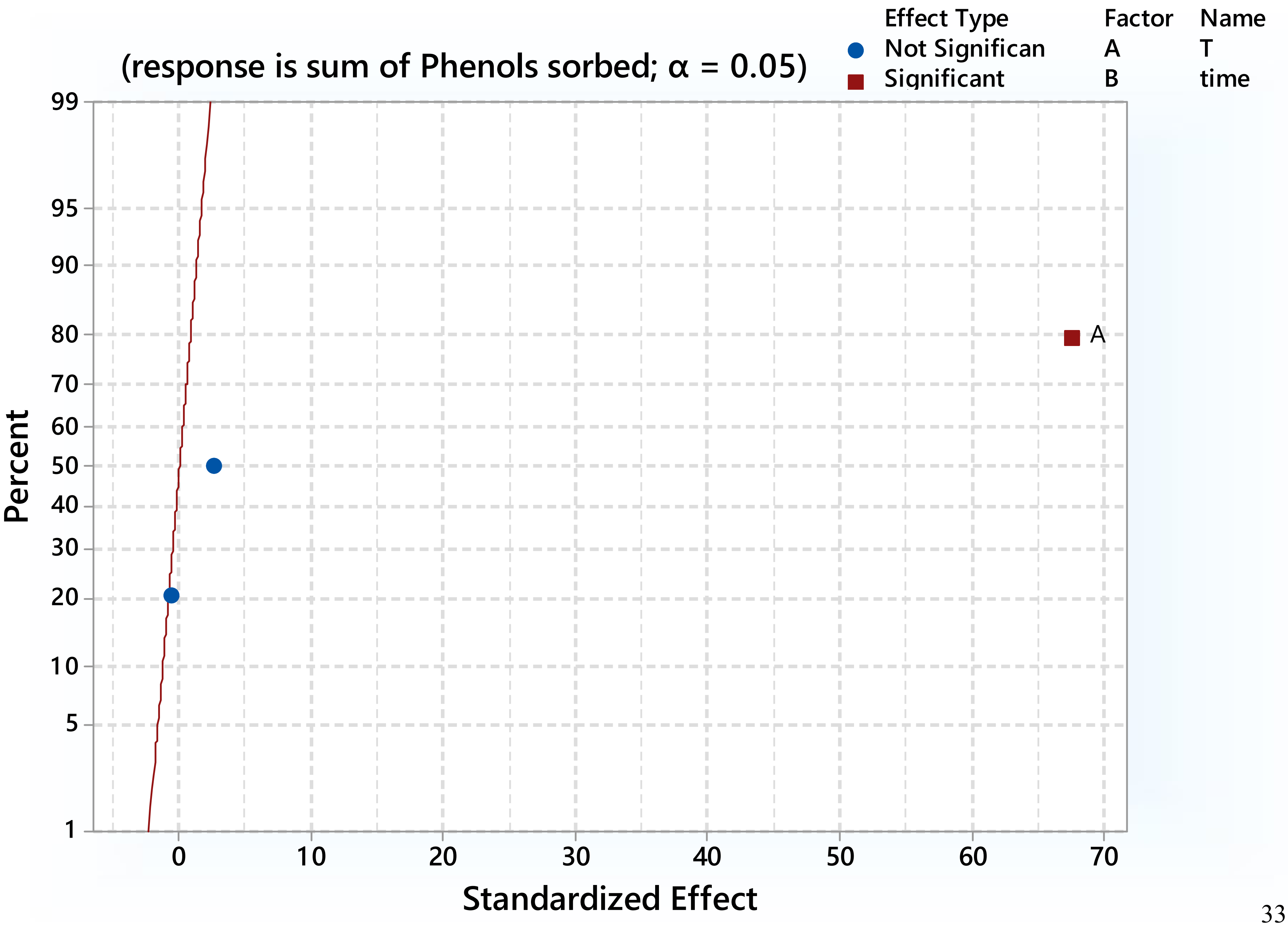

2-aminophenol
3-aminophenol
1-naphtol
2-naphtol
1-thymol
q (mg g-1)
0
50
100
150
200
250
300
350
400
450
ASAC1
ASAC2
ASAC3
ASAC4
ASAC5
ASAC6
ASAC7


2-nitrophenol
4-nitrophenol
cathecol
resorcinol
hydroquinone
q (mg g-1)
0
50
100
150
200
250
300
350
400
450
ASAC1
ASAC2
ASAC3
ASAC4
ASAC5
ASAC6
ASAC7



2-chlorophenol
o-cresol
m-cresol
4-methoxyphenol
bisphenol A
q (mg g-1)
0
50
100
150
200
250
300
350
400
450
ASAC1
ASAC2
ASAC3
ASAC4
ASAC5
ASAC6
ASAC7


(response is sum of Pharmaceuticals sorbed; α = 0.05)
Effect Type
Significant
Factor Name
A T
B time
Percent
99
95
90
80
70
60
50
40
30
20
10
5
1
A
AB
B
0
50
100
150
200
Standardized Effect



(response is sum of Phenols sorbed; α = 0.05)
Effect Type
Not Significan
Significant
Factor
A
B
Name
T
time
99
95
90
80
70
60
50
40
30
20
10
5
1
Percent
A
0
10
20
30
40
50
60
70
Standardized Effect

Lower total functional groups (AC-4 and AC-3)

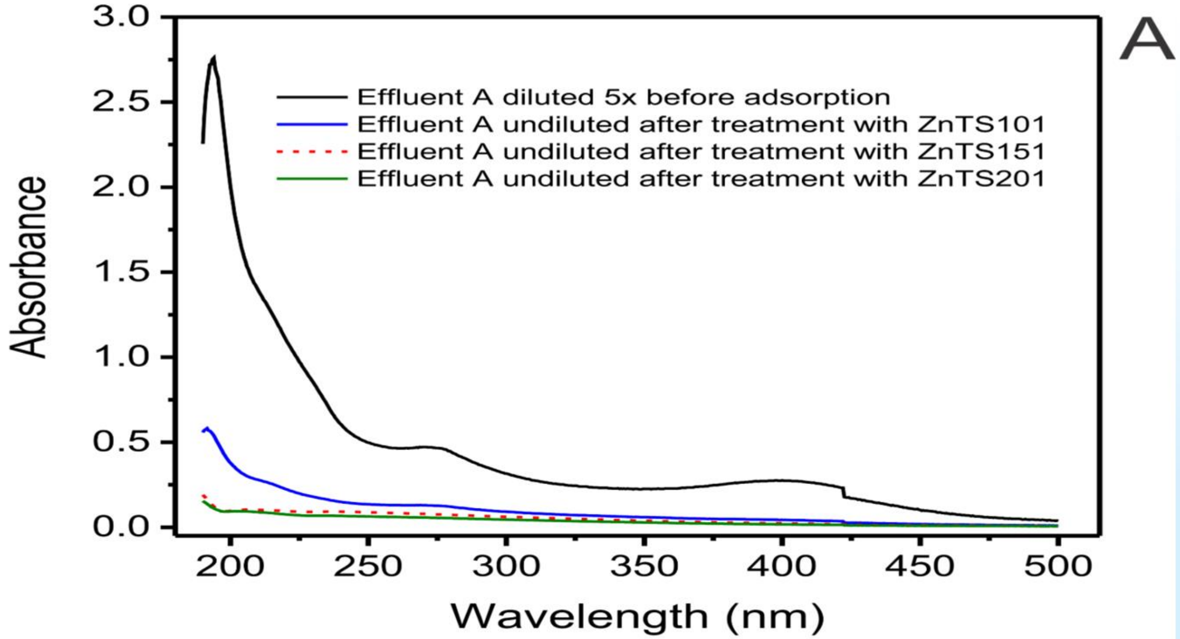
Higher sorption capacity of all organic compounds

Higher values of HI

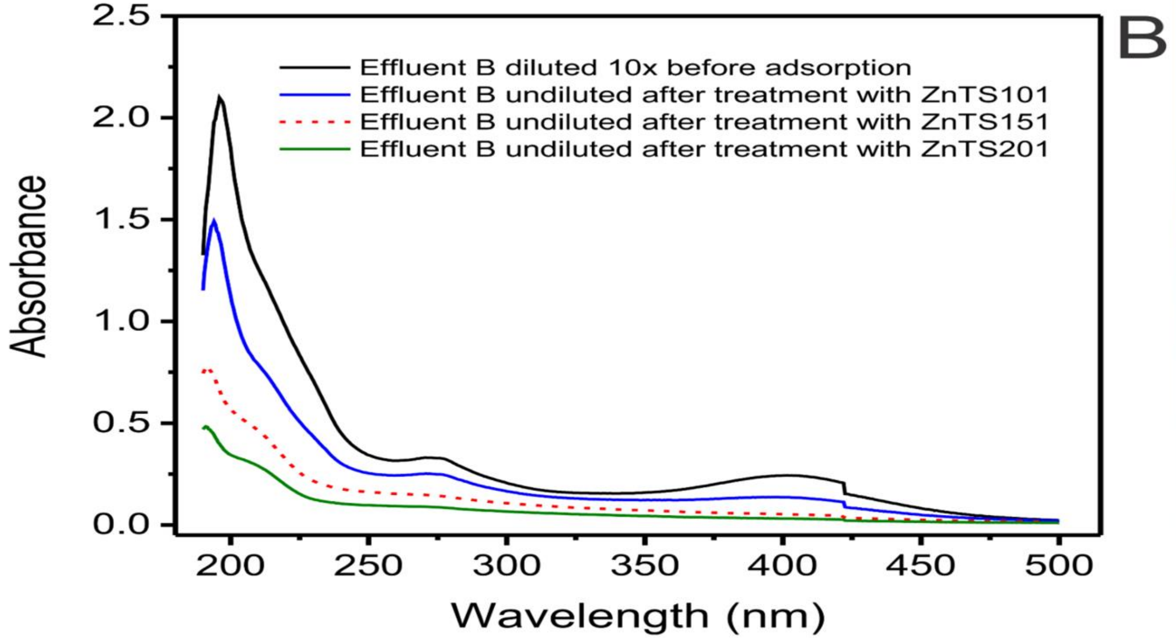
Therefore, making chemical reactions to increase the number Of functional groups onto activated carbon surface leads to a decrease in the sorption capacity of organic molecules Such as pharmaceuticals and Phenols

Chemical composition of synthetic industrial effluents.

	Concentration (mg L^{-1})	
Phenols	Effluent A	Effluent B
2- nitro-phenol	50	100
resorcinol	5	10
3-amino phenol	5	10
Phenol	5	10
o-cresol	5	10
m-cresol	5	10
2-chloro-phenol	5	10
bisphenol A	5	10
4- nitro-phenol	5	10
hydroquinone	5	10
Other Organic component		
humic acid	10	10
Inorganic components		
Sodium sulphate	20	20
Sodium carbonate	20	40
Sodium chloride	20	40
Potassium nitrate	20	40
Sodium phosphate	20	40
pH	7	7



ZnTS101	95.55%
ZnTS151	97.76%
ZnTS201	98.28%

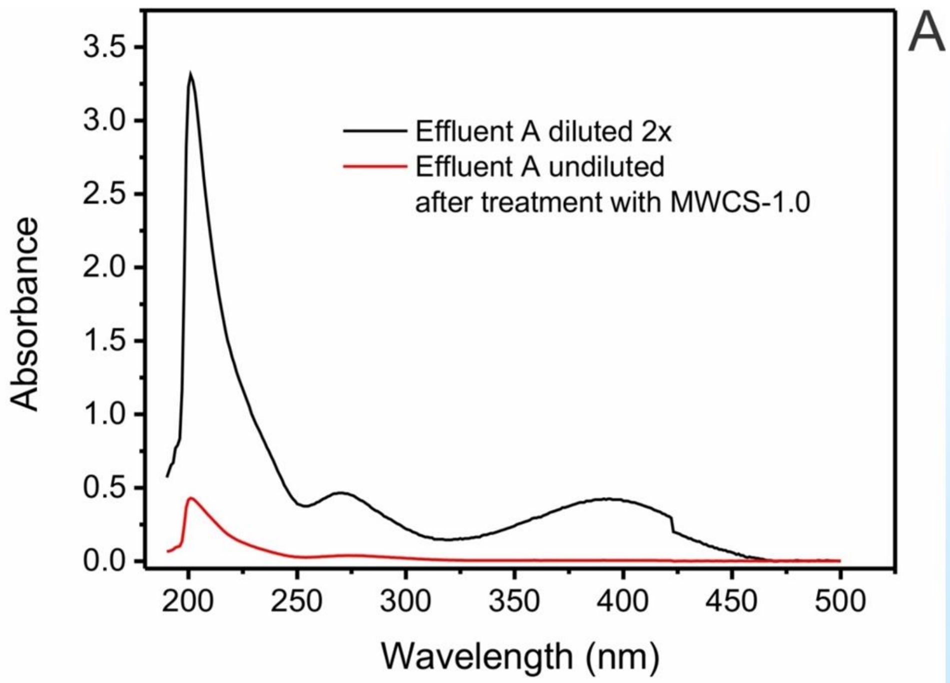


ZnTS101	93.25%
ZnTS151	96.30%
ZnTS201	97.74%

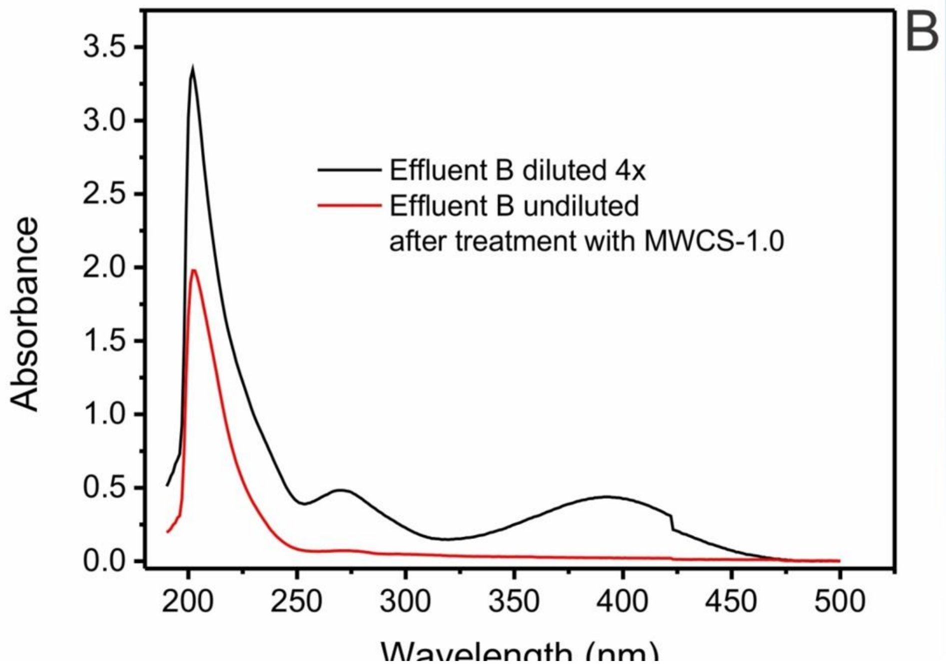
Chemical composition of simulated hospital effluents.

	Concentration (mg L^{-1})	
Pharmaceuticals	Effluent A	Effluent B
Diclofenac	20.0	40.0
Nimesulide	20.0	40.0
Amoxicillin	10.0	20.0
Acetyl salicylic acid	10.0	20.0
Sugars		
Saccharose	50.0	70.0
Glucose	30.0	40.0
Other Organic component		
Urea	20.0	40.0
Inorganic components		
Ammonium phosphate	20.0	30.0
Ammonium chloride	20.0	30.0
Sodium sulfate	50.0	70.0
Sodium chloride	50.0	70.0
Sodium carbonate	50.0	70.0
Sodium acetate	20.0	30.0
Magnesium carbonate	50.0	70.0
Potassium nitrate	10.0	20.0
pH*	8.0	8.0

*pH of hospital effluents.

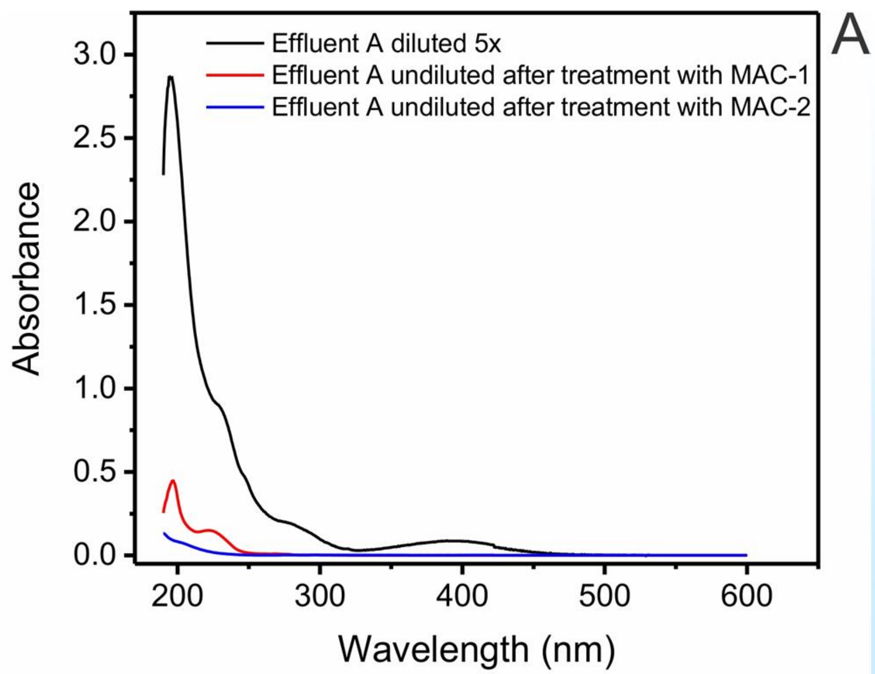


95.57% removal

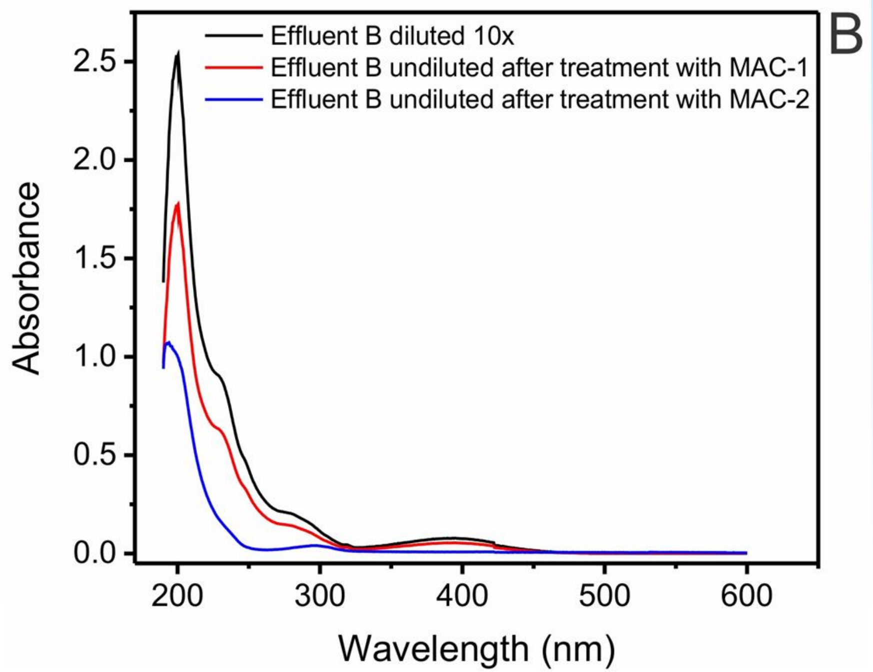


91.14% removal

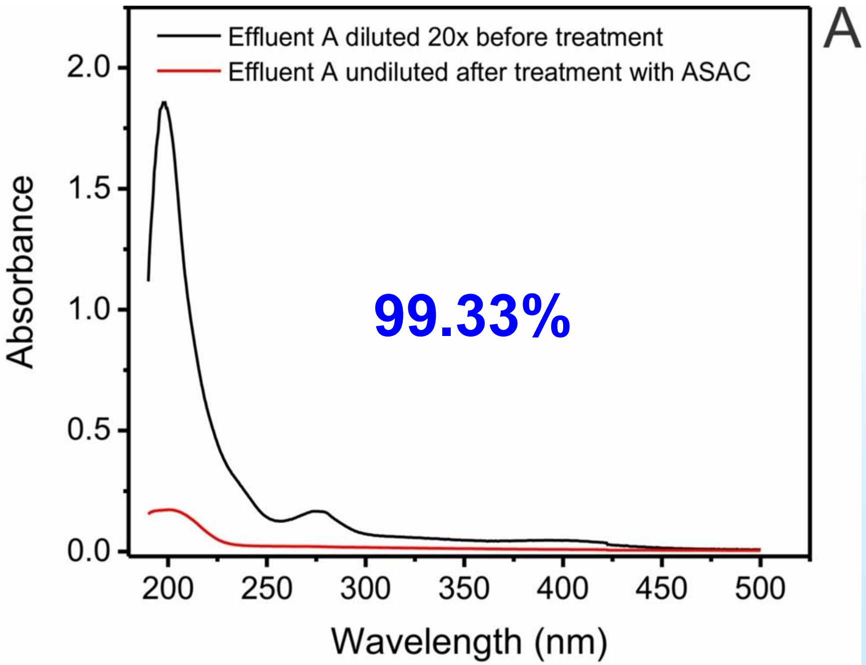
Concentration (mg L^{-1})		
Pharmaceuticals	Effluent A	Effluent B
Paracetamol	25.0	50.0
Amoxicillin	25.0	50.0
Diclofenac	10.0	20.0
Nimesulide	10.0	20.0
Acetyl salicylic acid	10.0	20.0
Sivastatin	10.0	20.0
Captopril	10.0	20.0
propranolol hydrochloride	10.0	20.0
enalapril maleate	10.0	20.0
Sugars		
Saccharose	30.0	50.0
Glucose	30.0	50.0
Other Organic component		
Urea	20.0	40.0
Citric acid	20.0	40.0
Inorganic components		
Ammonium phosphate	20.0	30.0
Ammonium chloride	20.0	30.0
Sodium sulphate	50.0	70.0
Sodium chloride	50.0	70.0
Sodium carbonate	50.0	70.0
Sodium acetate	20.0	30.0
Magnesium carbonate	50.0	70.0
Potassium nitrate	10.0	20.0
pH*	7.0	7.0

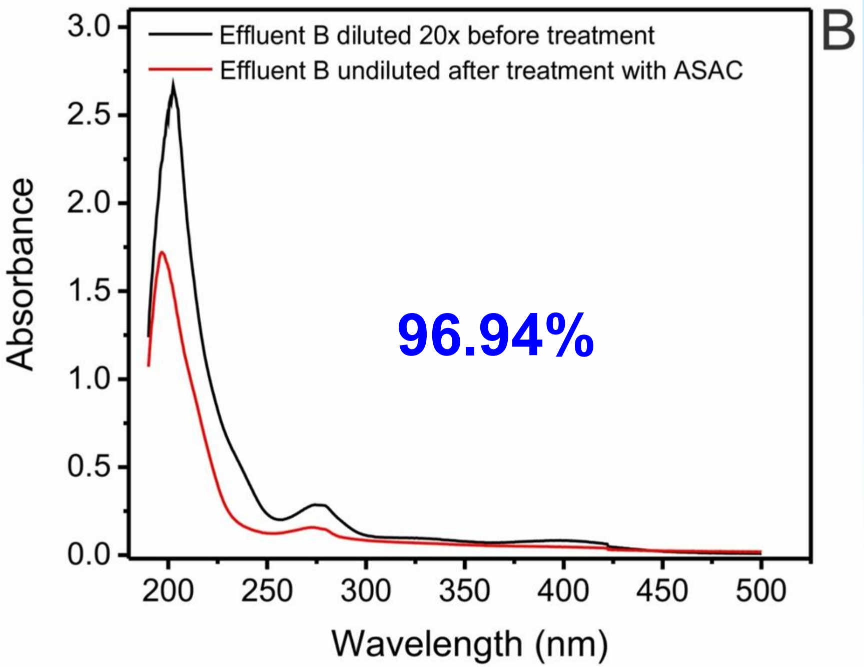


	% Removal
MC-1	97.95%
MC-2	99.41%



	% Removal
MC-1	93.00%
MC-2	96.77%





	Concentration (mg L^{-1})	
Phenols	Effluent A	Effluent B
Resorcinol (RES)	50.00	100.0
3-amino phenol (AMP)	50.00	100.0
Phenol	5.00	10.0
2-cresol	5.00	10.0
3-cresol	5.00	10.0
2-chloro-phenol	5.00	10.0
Bisphenol A	5.00	10.0
2- nitro phenol	5.00	10.0
4- nitro phenol	5.00	10.0
2-Naphtol	5.00	10.0
Hydroquinone	5.00	10.0
Organic Matter		
Humic Acid	10.0	20.0
Inorganic components		
Sodium sulphate	20.0	40.0
Sodium carbonate	20.0	40.0
Sodium chloride	20.0	40.0
Potassium nitrate	20.0	40.0
Potassium phosphate	20.0	40.0
pH*	7.0	7.0

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Thank you very much

for your special attention