International Conference on:

Pollution Control & Sustainable Environment

Water treatment containing organic compounds by coupling adsorption and electrochemical degradation at BDD anode: Sawdust adsorption performance for the treatment of dilute phenol solutions

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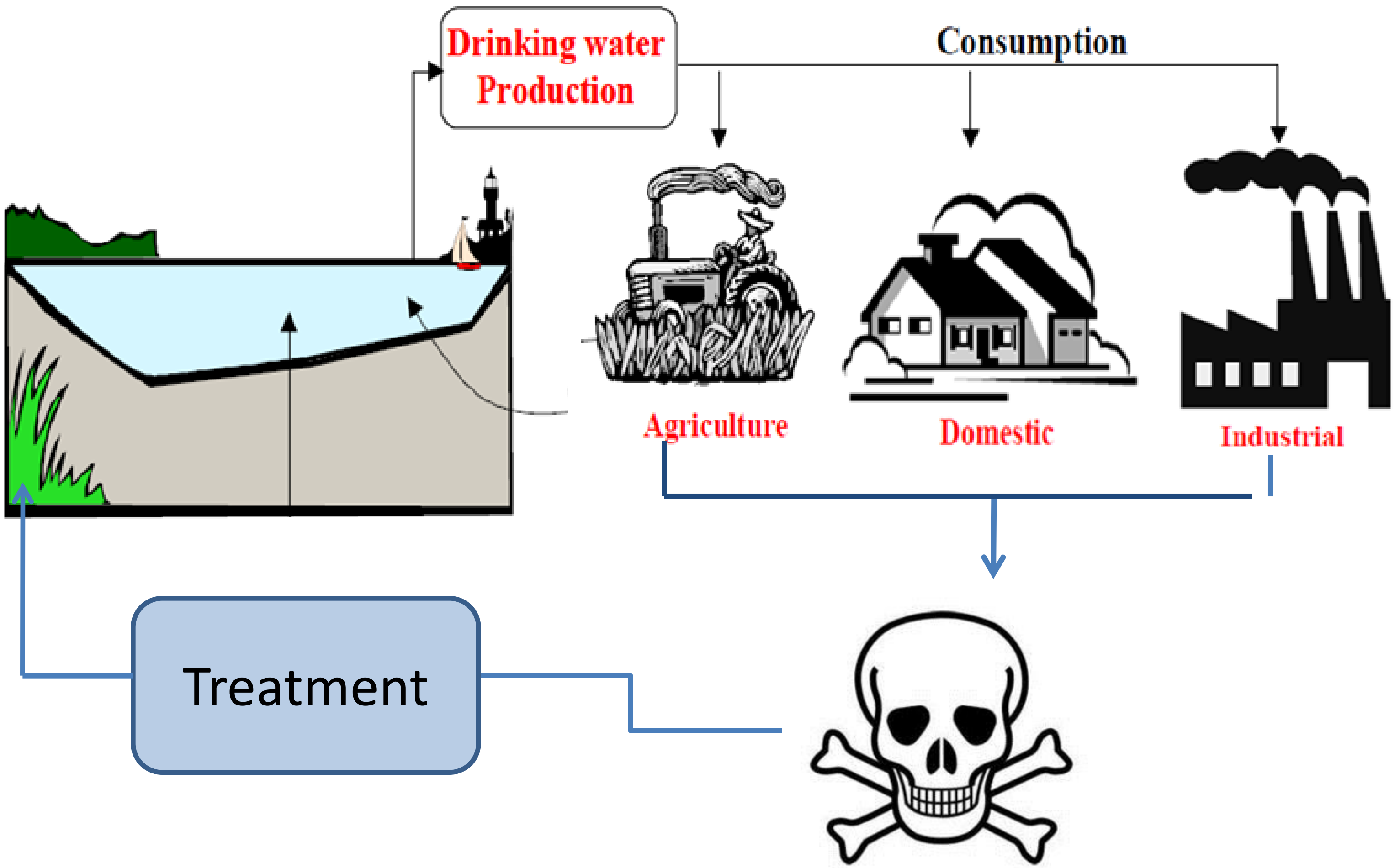
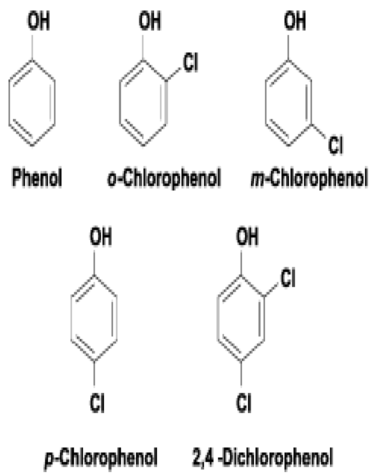

Drinking water Production
Consumption
Agriculture
Domestic
Industrial
Treatment



Phenolic compounds

- ***Origin :pharmaceutical, pesticides, oil, textiles, painting, dyes, plastic, detergent industries …***

- ***Dangers:***
  - ***Highly toxic,***
  - ***highly oxygen demanding,***
  - ***Carcinogenic, mutagenic, and can cause a severe health hazard to human beings.***

Biological methods

Phenolic compounds are generally Non-biodegradable

- Main reagent : the electron
- Complete oxidation (Mineralization) : possible
- Transformation of organic pollutants into biodegradable products: possible

Chemical methods

Waste water treatment processes

Physical methods

☹ cost, secondary waste …

Electrochemical methods

Electrochemical methods

Degradation of organic compounds(R)

First Step: $H_2O \rightarrow OH^{\bullet} + H^+ + e^-$

Second Step: $R \xrightarrow{OH^{\bullet}}$ Biodegradable compounds $+ CO_2$

Anode material

Choice of the anode material: high oxygen overpotential

Competing Reactions:

$$H_2O \rightarrow \frac{1}{2} O_2 \uparrow + 2H^+ + 2e^-$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

Overvoltage for different anode materials, 1 A m-2 in sulfuric acid

Anode material	Pt	PbO_2	SnO_2	BDD
Overpotential (V)	0,27	0,50	0,67	1,27

Electrochemical methods

Low current efficiency for the treatment of dilute solutions

Mass transfer limitations → Not economically viable

Coupling of electrochemical processes with a pre-concentration step is needed

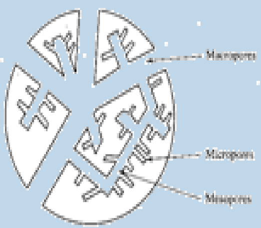
How?

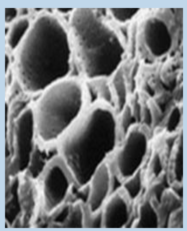
Adsorption- electochemical oxidation coupling

OBJECTIVE OF THE WORK

Adsorbents

Commercial activated carbon





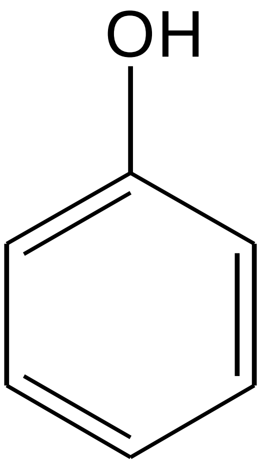
Origin: wood
Particles size: 0.4 mm
Specific area: 980 m^2/g
PH_{PZC}= 8,9

Red wood sawdust

Origin : Coniferous trees
(by-product of furniture industry)
Specific area: 0.4 m^2/g
Particles size: 0.5-1.12 mm

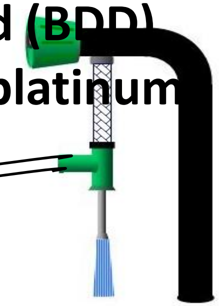
Model compound

Phenol



Experimental setups

- **Batch adsorption**
- **Column adsorption**
- **Electrochemical degradation**



Conditions:

- ❖ **Anode: boron-doped diamond (BDD)**
- ❖ **Cathode: cylindrical mesh of platinum**
- ❖ **Electrolyte: Na_2SO_4**

Analytical techniques

- **High Performance Liquid Chromatography (HPLC)** → **Phenol and its oxidation intermediates**

Characterization of adsorbents

- **Automated gas sorption system** → **BET surface**
- **Cyclic voltammetry** → **Electrochemical behavior of the activated carbon paste**

General approach

Adsorption

Desorption

Electrolysis

- Kinetics study
- adsorption isotherms
- Saturation of adsorbents

- Study of the polluta
desorption without polarization
- Study of the pollutants
desorption under pola

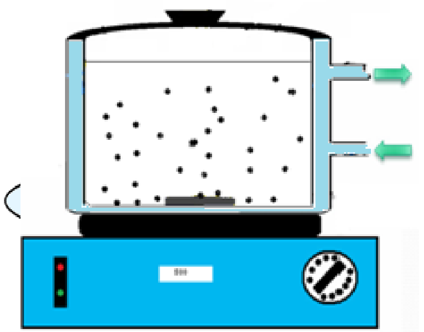
Electro-oxidation of pollutants

Electrochemical regeneration of adsorbent

Desorption studies

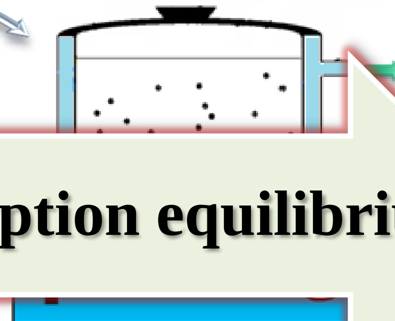
Quantify the long term desorption without polarization.

- **Simple desorption**
- **Multiple desorption**



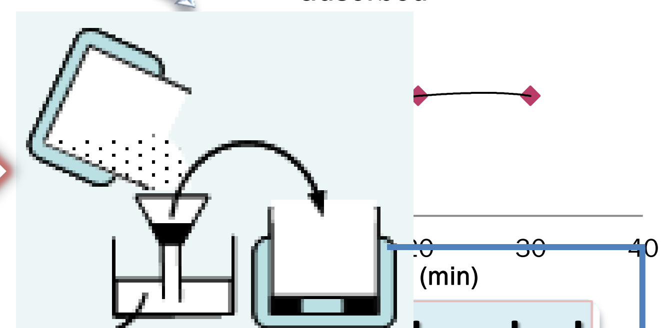
Stirring

Desorption equilibrium



Stirring

Desorption kinetic of phenol adsorbed



Dosage of desorbed pollutant

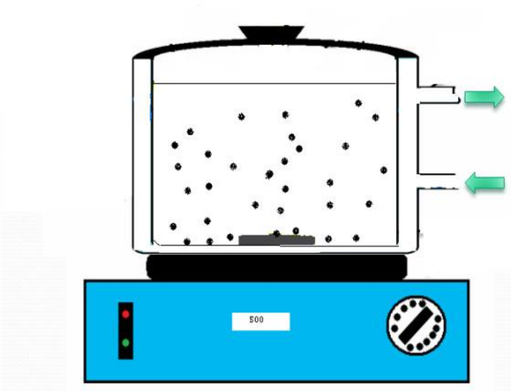
In the case of sawdust : Solution used : Na_2SO_4 (neutral pH)

Volume of the solution for each step = 1/4 of the simple desorption volume

In the case of activated

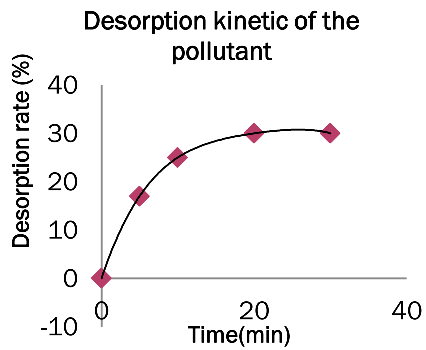
The process was repeated 4 times

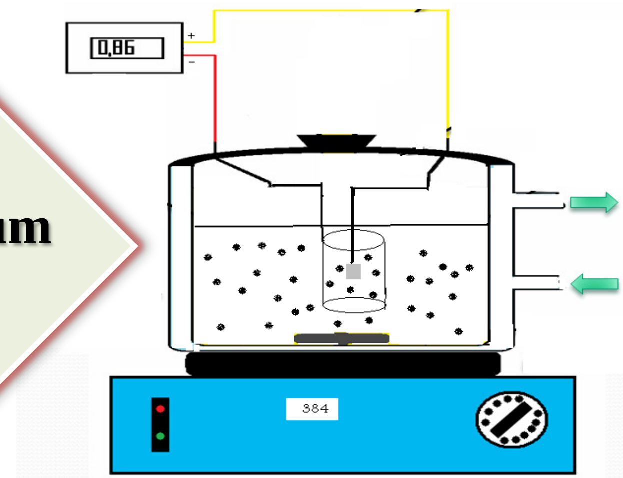
Electrochemical degradation of phenol



Desorption of the pollutant

Desorption equilibrium



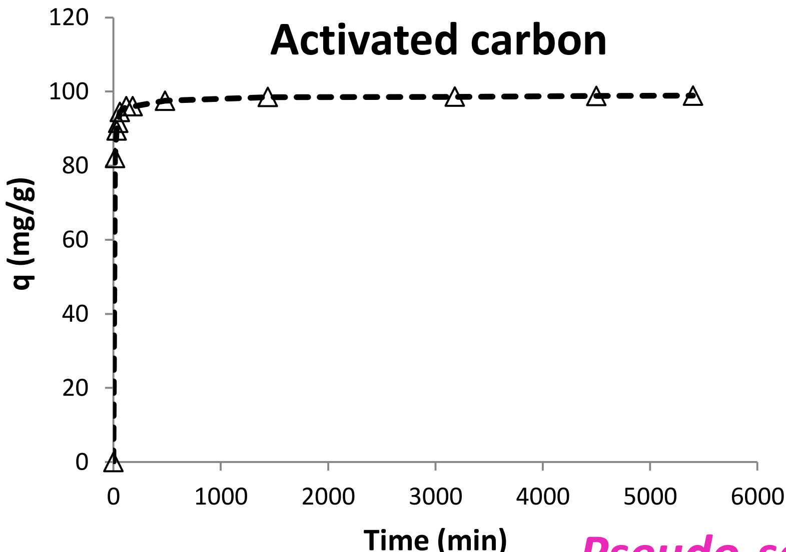


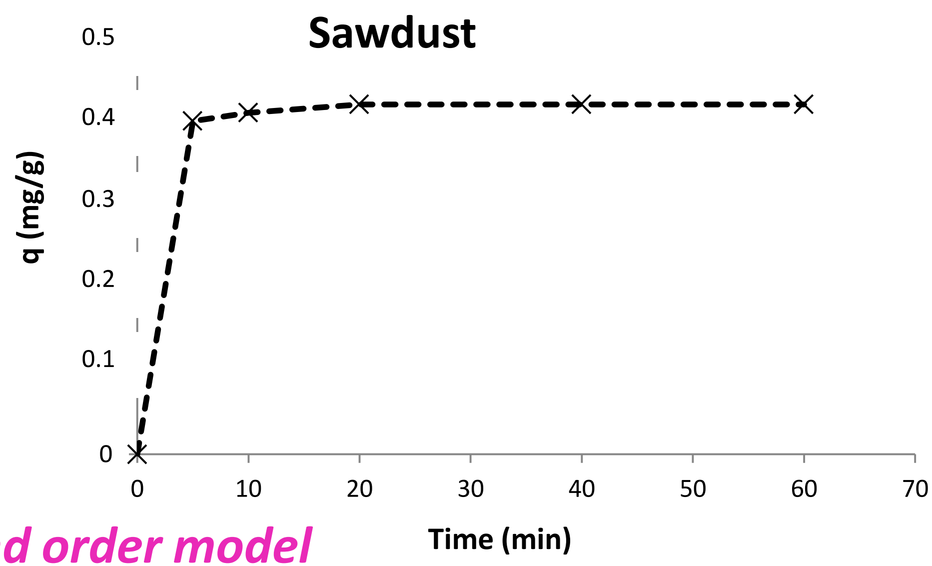
Electrochemical degradation

Electrolysis conditions:

- ❖**Anode: BDD**
- ❖**Cathode: cylindrical mesh of platinum**
- ❖**Electrolyte: Na_2SO_4 (0,1M) of desired pH**

Adsorption kinetics of phenol onto activated carbon and sawdust





Pseudo-second order model

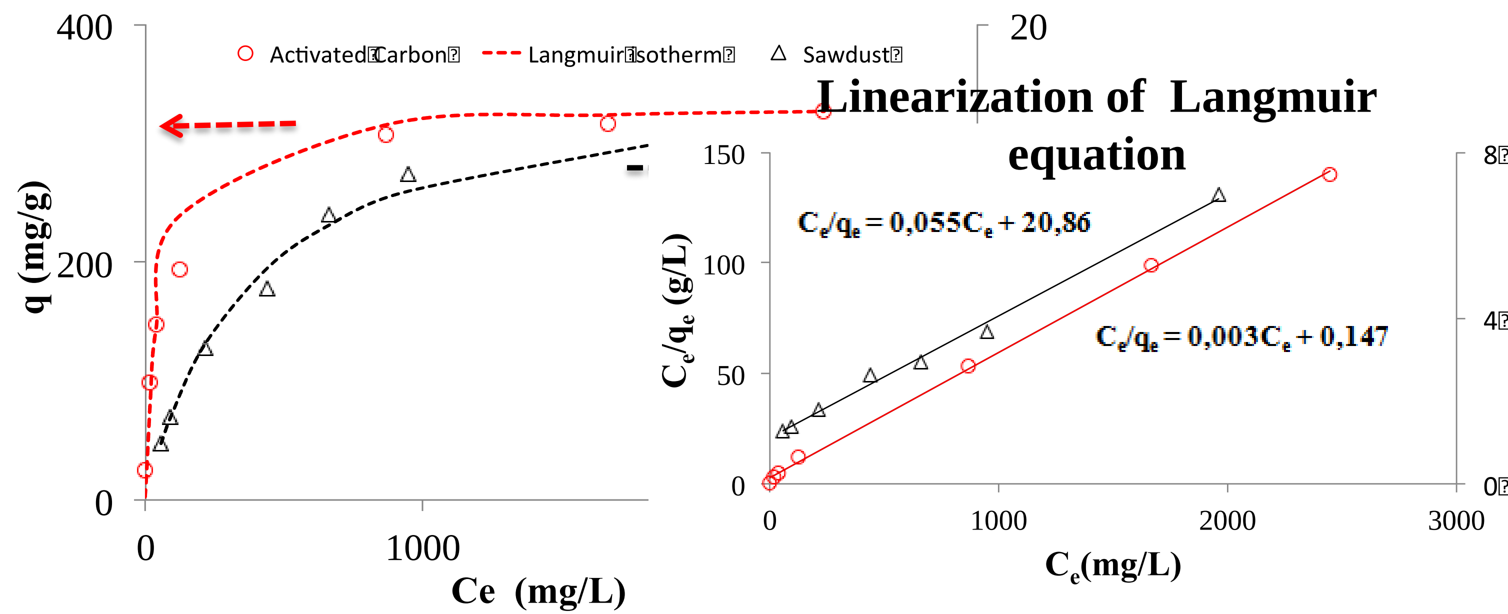
- Activated carbon: equilibrium time=3 days
- Sawdust: equilibrium time=20 min

The phenol adsorption follows a pseudo-second order kinetic for both adsorbents

Inte... phenol in the pores of activated carbon reduces the pollutant scaveng... the activated carbon adsorption sites.

Adsorption isotherms of phenol at 30°C

Linearization of Langmuir equation



$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

Equilibrium data are well represented by the Langmuir isotherm equation.

C_e : equilibrium concentration of the adsorbate (mg/L)

q_e :adsorption capacity (mg g^{-1}),

q_m : maximum adsorption capacity (mg g^{-1})

K_L : Langmuir isotherm constant (L mg^{-1}).

Adsorption isotherms of phenol at 30°C

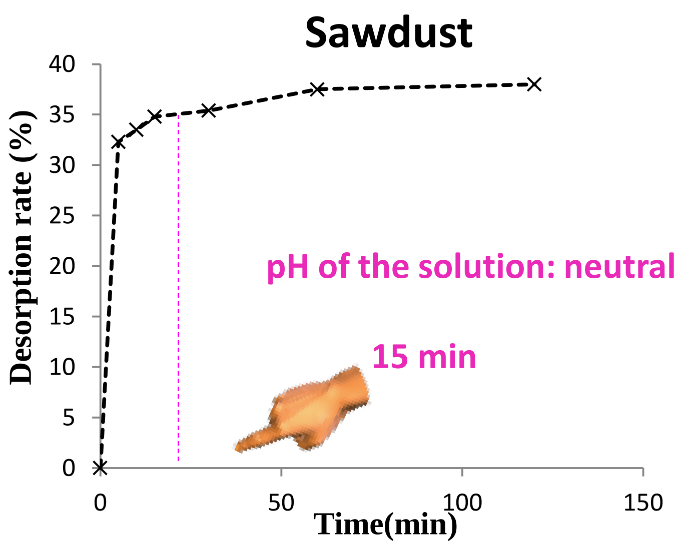
Adsorbent	Langmuir constants		q_m/S (mg/m^2)
	q_m (mg/g)	K_L (L/mg)	
Sawdust $S = 0.4\ m^2/g$	18,2	0,003	45,5
Activated carbon $S = 980\ m^2/g$	333,3	0,02	0,3

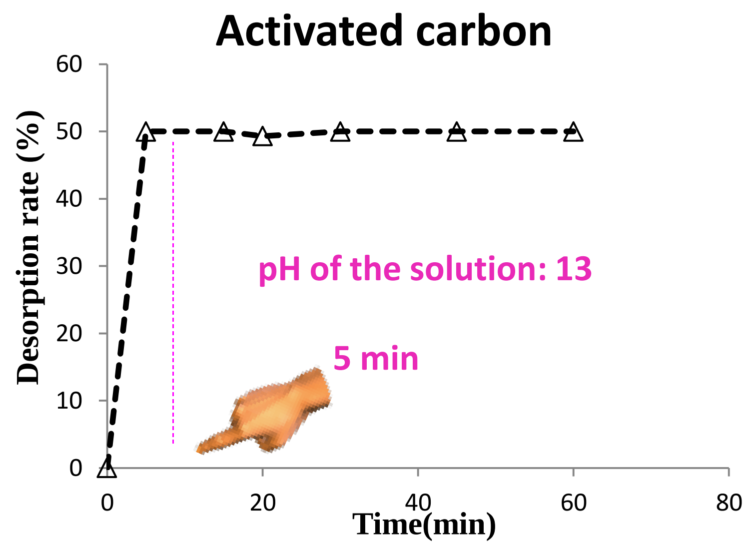
q_m of the activated carbon is the highest ➔ **Activated carbon has the highest specific surface**

➔ **The sawdust is capable to adsorb a higher phenol weight per surface unit**

Phenol desorption

Desorption kinetics of phenol





In the case of activated carbon: maximum desorption rate =50%

The desorption kinetics of the phenol is very fast

In the case of sawdust: maximum desorption rate=38%

The phenol retained by the activated carbon comes in two states: strongly adsorbed (chemisorption)and weakly adsorbed (physisorption)

Value relatively high : phenol is still in its undissociated form

Hypothesis: an important part of phenol retained on sawdust is rather weakly adsorbed

Solution of pH 13

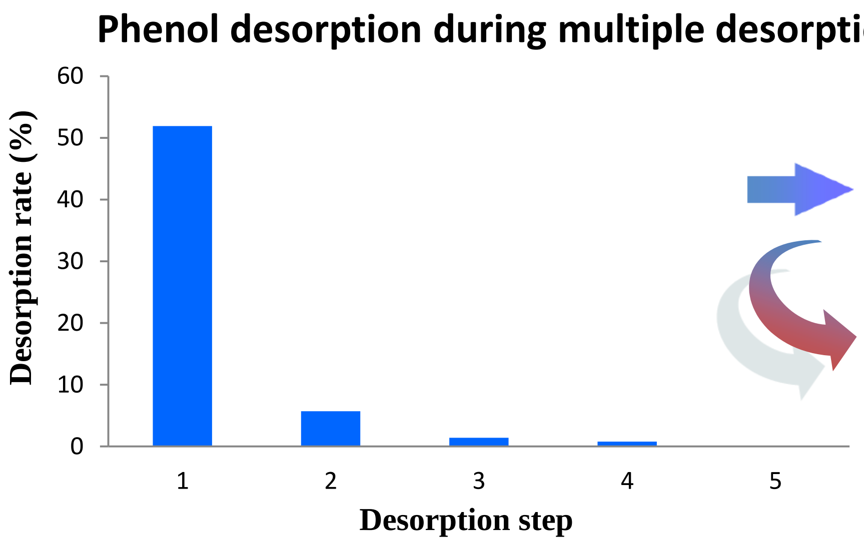
$pH > pK_a + 1$

Activated carbon

$pH > pH_{PZC}$

Phenol desorption

Multiple desorption



The % of the desorbed phenol does not exceed 60%

A part of the phenol adsorption is rather chemical and irreversible

Re-adsorption of phenol on activated carbon obtained after multiple desorption

$$E(\%) = \frac{\text{Adsorptive capacity of the activated carbon after multiple desorption steps}}{\text{Initial adsorption capacity of the fresh activated carbon}} * 100$$

Regeneration efficiency : E = 73%

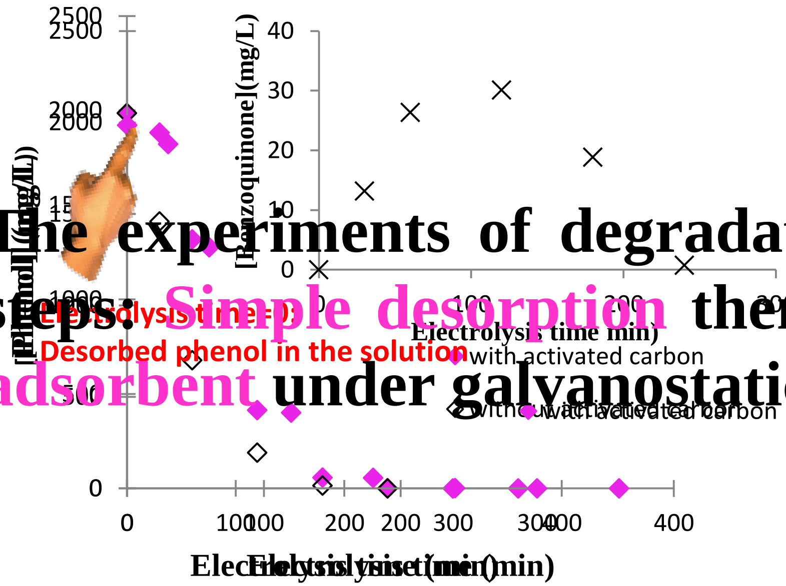
E obtained (73%) is higher than expected (60%)

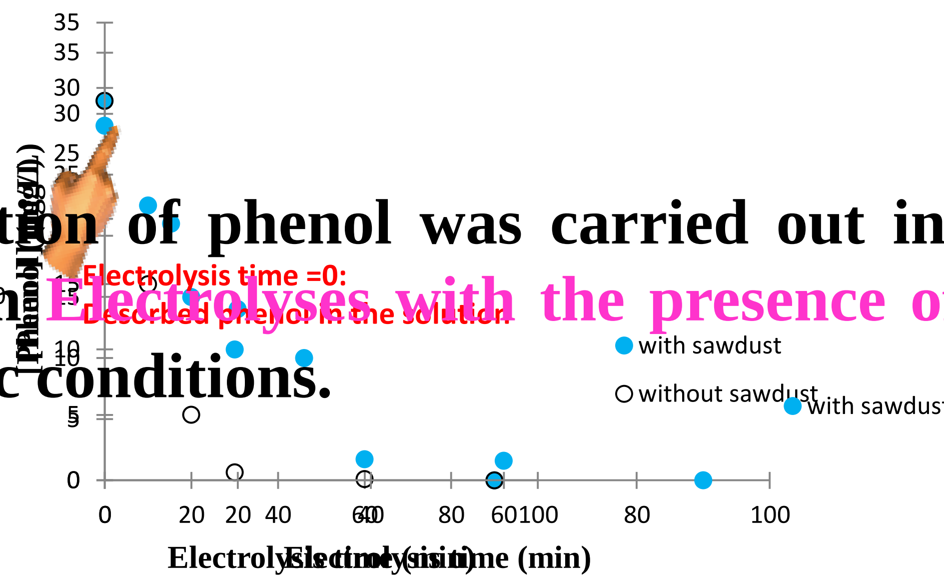
- Changes in the properties of activated carbon after contact with NaOH during the desorption
- Fragmentation of the activated carbon particles by stirring

Electrochemical degradation of phenol

Oxydation of phenol on BDD anode at i=0.215 A/cm^2

The experiments of degradation of phenol was carried out in two steps: Simple desorption then Electrolyses with the presence of the adsorbent under galvanostatic conditions.





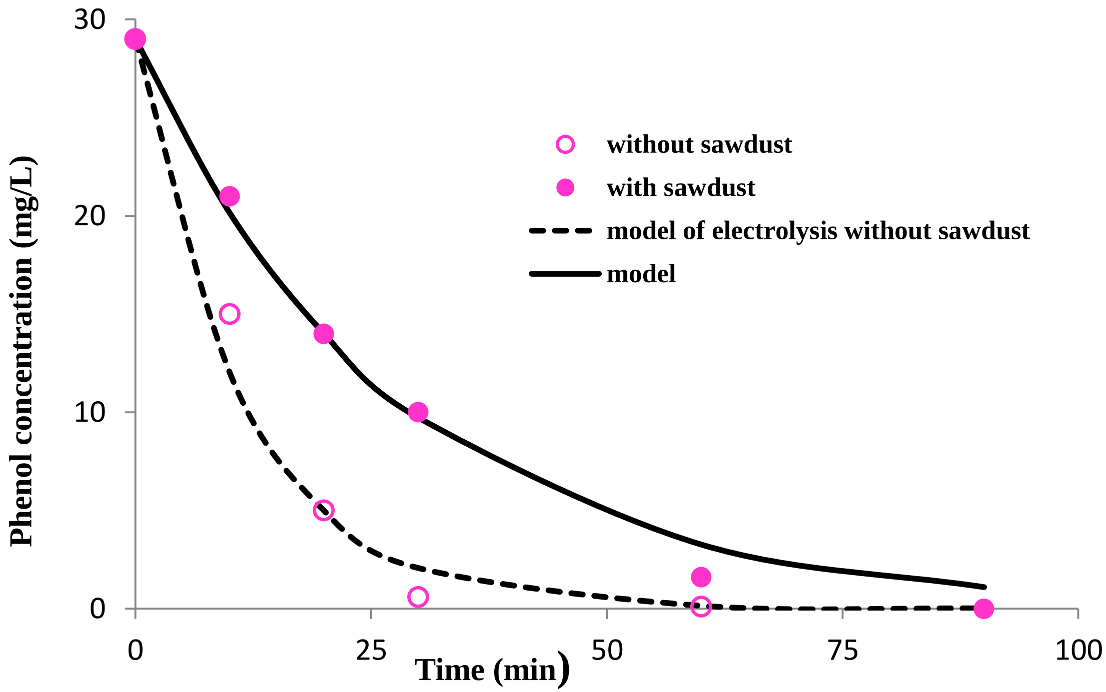
The total disappearance of the phenol is achieved in the presence of adsorbents

The rate of disappearance of phenol alone > that in the presence of the adsorbent

A part of the initially adsorbed phenol was desorbed during electrolysis.

Electrochemical degradation of phenol

Modeling of phenol degradation in the presence of sawdust



$$C = C^{\circ} exp \left\{ (k_{des} - \frac{k * S}{V}) t \right\}$$

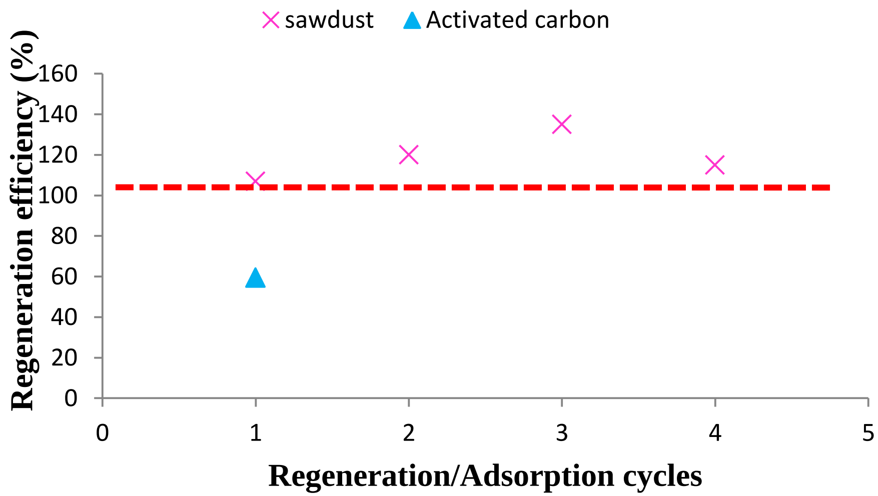
k= 0.0252 m.min^{-1}

k_{des}= 0.0516 min^{-1}

Adsorption/electrochemical regeneration cycles

Regeneration efficiency (Re) → **(1) Initial adsorption + (2) Electrochemical degradation + (3) Re-adsorption**

Adsorption/Regeneration Cycles → **Repetition: (2) Electrochemical degradation + (3) Re-adsorption**



Electrolysis conditions: i=0.215 A/cm²
electrolysis time=5 hours

Phenol/sawdust couple
Phenol/activated carbon couple

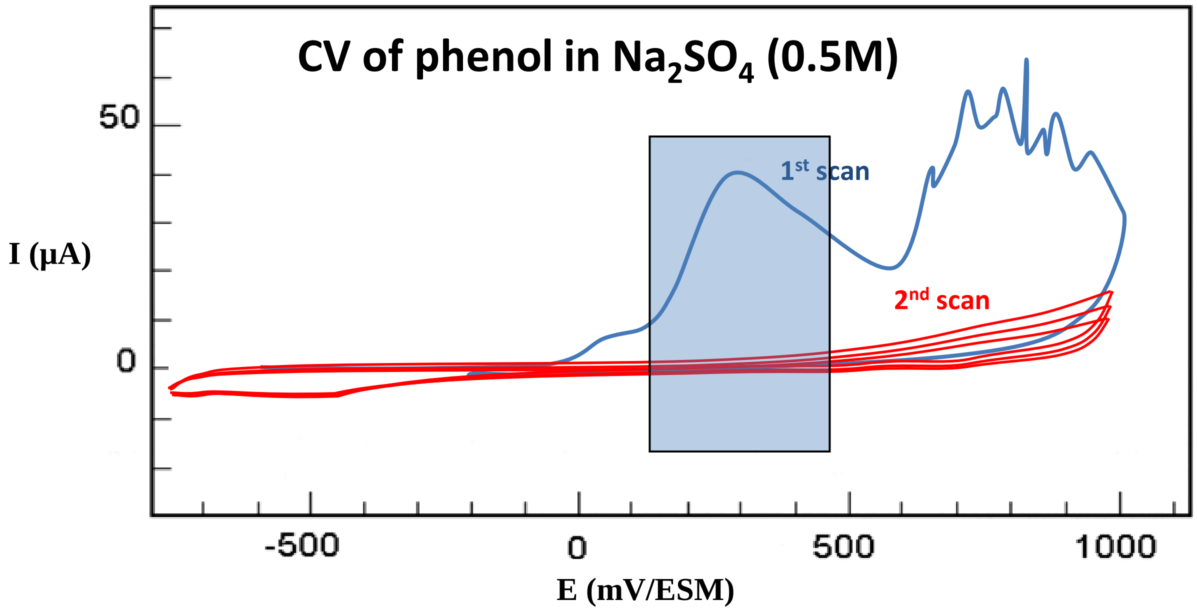
Regeneration efficiency> 100 % after four cycles
Regeneration efficiency= 59,5 %

Sawdust is more easily regenerated because of its surface properties unlike activated carbon
The remaining chemisorbed phenol is not affected by the electrochemical regeneration

A possible electro-polymerization of the phenol at the boundary of the activated carbon pores
Electrochemical treatment seems to activate sawdust by changing its physicochemical properties

Electrochemical behavior study of activated carbon by cyclic voltammetry

Oxidation of phenol solution on a virgin activated carbon paste



- The oxidation pic of phenol disappears completely from the second cycle

Electro-polymerization of phenol on the surface of activated carbon

Electrochemical behavior study of activated carbon by cyclic voltammetry

Electrolyte oxidation on an activated carbon (obtained after multiple desorption) paste electrode

CV of electrolyte Na_2SO_4 (0,5M)

50

I (µA)

0

1^{st} scan

0

500

E (mV/ESM)

Hypothesis confirmed: the electropolymerization of the strongly adsorbed phenol can explain the deterioration in performance of activated carbon by the obstruction of its pores during the electrolysis.

The Search of other nonconductive adsorbents

Sawdust

- The oxidation ... ol disappears completely during the following cycles

The deactivation of the activated carbon could be associated to the electropolymerization of the phenol strongly retained by the activated carbon

Conclusion

Adsorption study:

- ***Both adsorbents (activated carbon and sawdust) follow a Langmuir adsorption isotherm.***

- ***The maximum adsorption capacity of the activated carbon is 18 times greater than the one obtained with sawdust.***

Desorption study:

- ***An important part of phenol retained on the activated carbon is rather irreversible.***

- ***An important part of phenol retained on the sawdust is rather weakly adsorbed.***

Conclusion

- ***Electrochemical regeneration study:***

- ***The regeneration efficiency of the activated carbon is only 59% after 1 cycle of adsorption and regeneration:***
  - ***Low reversibility of the adsorption.***
  - ***Electropolymerization of the phenol on the surface of the activated carbon during anodic electrolysis***

- ***The regeneration efficiency of sawdust is more than 100% at the end of the fourth adsorption-regeneration cycle:***
  - ***Sawdust is easily regenerated because of its surface properties.***
  - ***Electrochemical treatment seems to activate sawdust by changing its physiochemical properties.***

Perspectives

- **Understanding the mechanism of sawdust activation.**
- **The application of this method on other types of organic pollutants.**
- **Studying the competition of several organic compounds which may be present in a real effluent on their abilities to be adsorbed, desorbed and oxidized.**
- **Development of a reactor (adsorption+regeneration):**

Publications

I. Bouaziz, C. Chiron, R. Abdelhedi, A. Savall, K. Groenen Serrano, Treatment of dilute methylene blue-containing wastewater by coupling sawdust adsorption and electrochemical regeneration, Environ. Sci. Pollut. Res., 2014, 21, 8565-8572.

I. Bouaziz, M. Hamza, R. Abdelhedi, A. Savall, K. Groenen Serrano, Treatment of diluted solutions of methylene blue by adsorption coupled with electrochemical regeneration: a comparative study of three adsorbents, ECS Trans., 2014, 59(1), 495-502.

Thank you