The effect of nanobubbles on heavy metal ions adsorption by activated carbon produced from lignite

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2014-2020
ανάπτυξη - εργασία - αλληλεγγύη
Partnership Agreement
2014 - 2020

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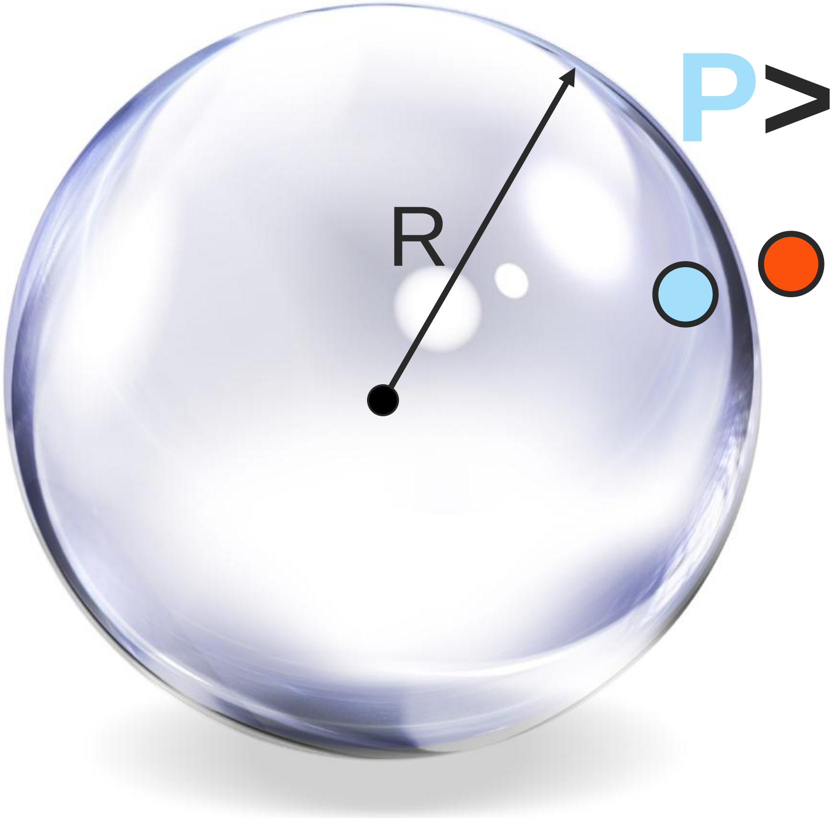
Nanobubbles: Are they exist?



$P > p$=1 bar

$$\Delta P = \frac{2\sigma}{R}$$

σ=70 mN/m

R=1 mm	P=1.0014 bar
R=1 µm	P=2.4 bar
R=100 nm	P=15 bar

Timeline of nanobubbles

P.S. Epstein and M.S. Plesset
On the stability of gas bubbles in liquid-gas solutions
Journal of Chemical Physics **18**, 1505 (1950)

N. Ishida et al.
Nanobubbles on a hydrophobic surface in water observed by tapping-mode atomic force microscopy
Langmuir **16**, 6377 (2000)

K. Ohgaki et al.
Physicochemical approach to nanobubble solutions
Chemical Engineering Science **65**, 1296 (2010)

M. Alheshibri et al.
A History of Nanobubbles
Langmuir **32**, 11086 (2016)

Bubbles in literature

Herodotus: Book III (Thalia): 23 (4th century BC)

He mentions a fountain containing a special kind of water in the land of the Macrobians, which gives the Macrobians their exceptional longevity. The water was so weak that nothing would float in it, neither wood, nor any lighter substance…

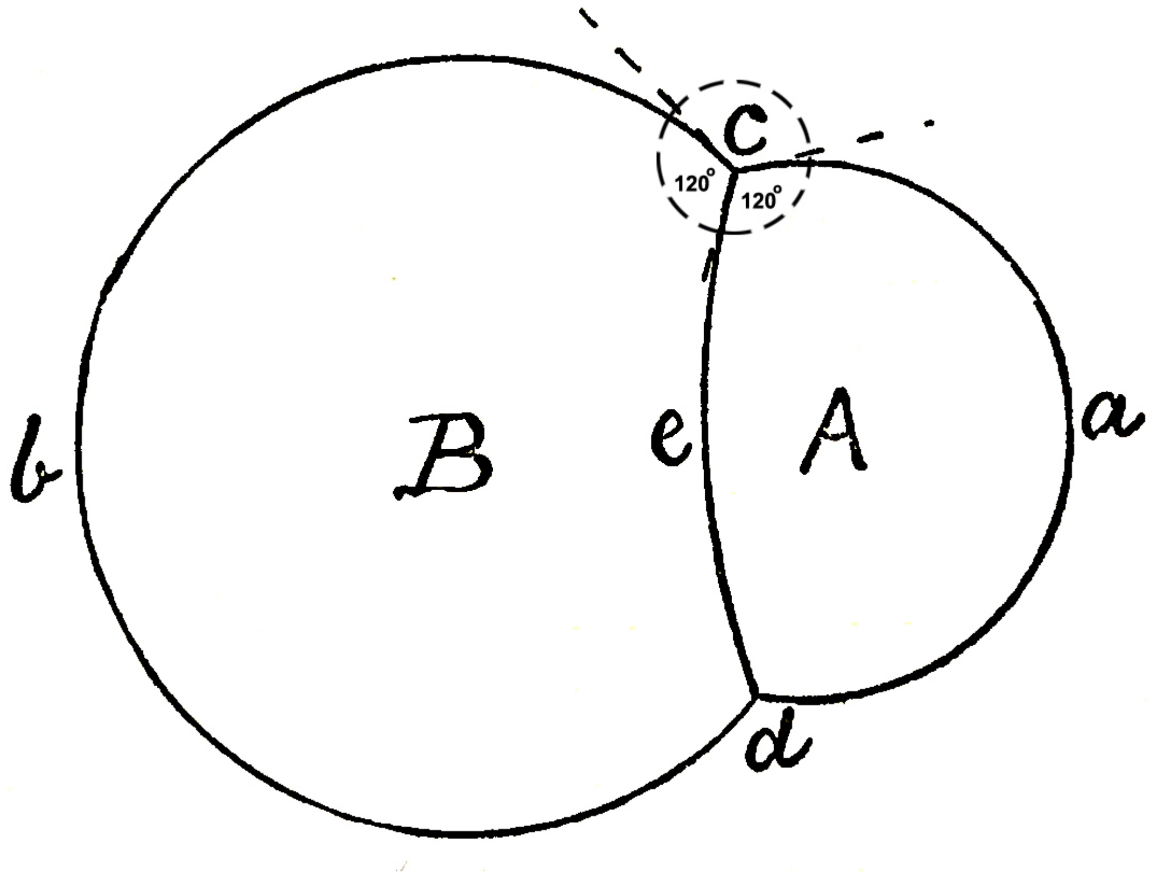
Nathaniel Hawthorne: Dr. Heidegger's Experiment (1837)

While he spoke Dr. Heidegger had been filling the four champagne-glasses with the water of the Fountain of Youth. It was apparently impregnated with an effervescent gas, for little bubbles were continually ascending from the depths of the glasses and bursting in silvery spray at the surface…

Gerard Liger-Belair et al.: J. Food Eng. **163**, 60 (2015)

They reported 150 nm bubble nucleation in champagne.

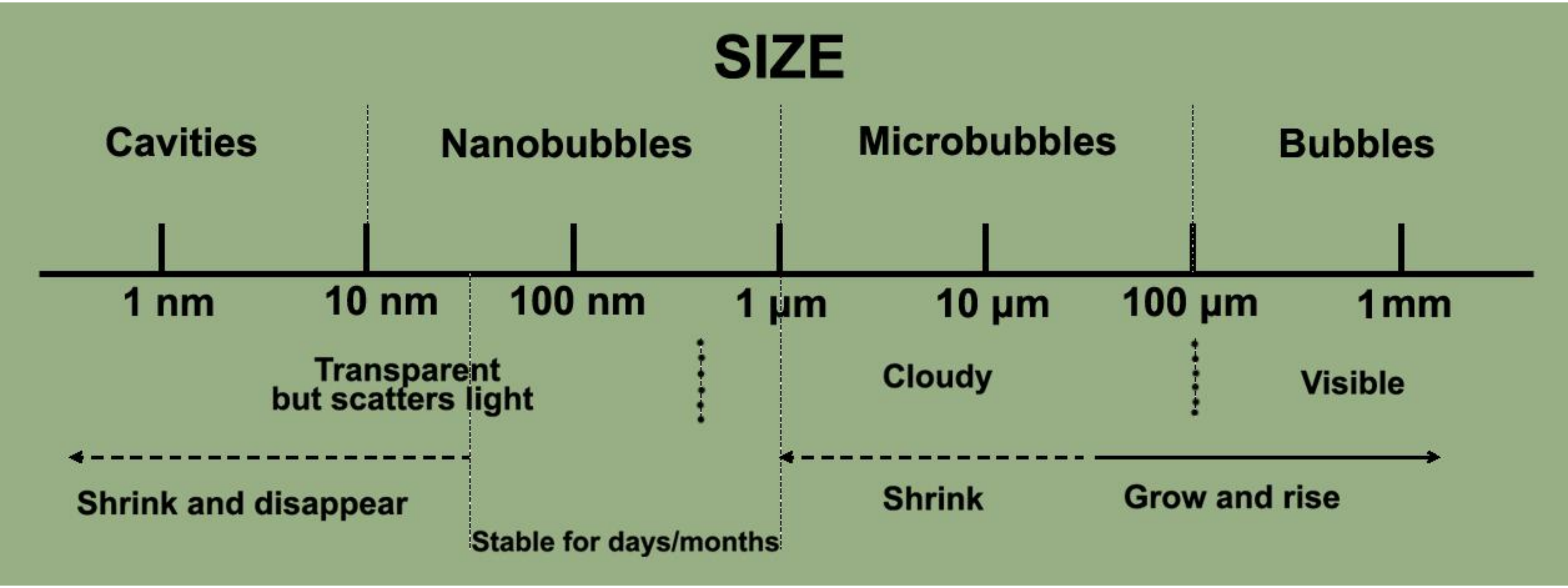
Composite bubbles



$$\frac{1}{A} = \frac{1}{B} + \frac{1}{e}$$

Sir Charles Vernon Boys soap-bubbles p.120, London (1916).

Bubble classification



Further classification:

1) SNB: Surface nanobubbles and 2) BNB: Bulk nanobubbles

Ostwald ripening

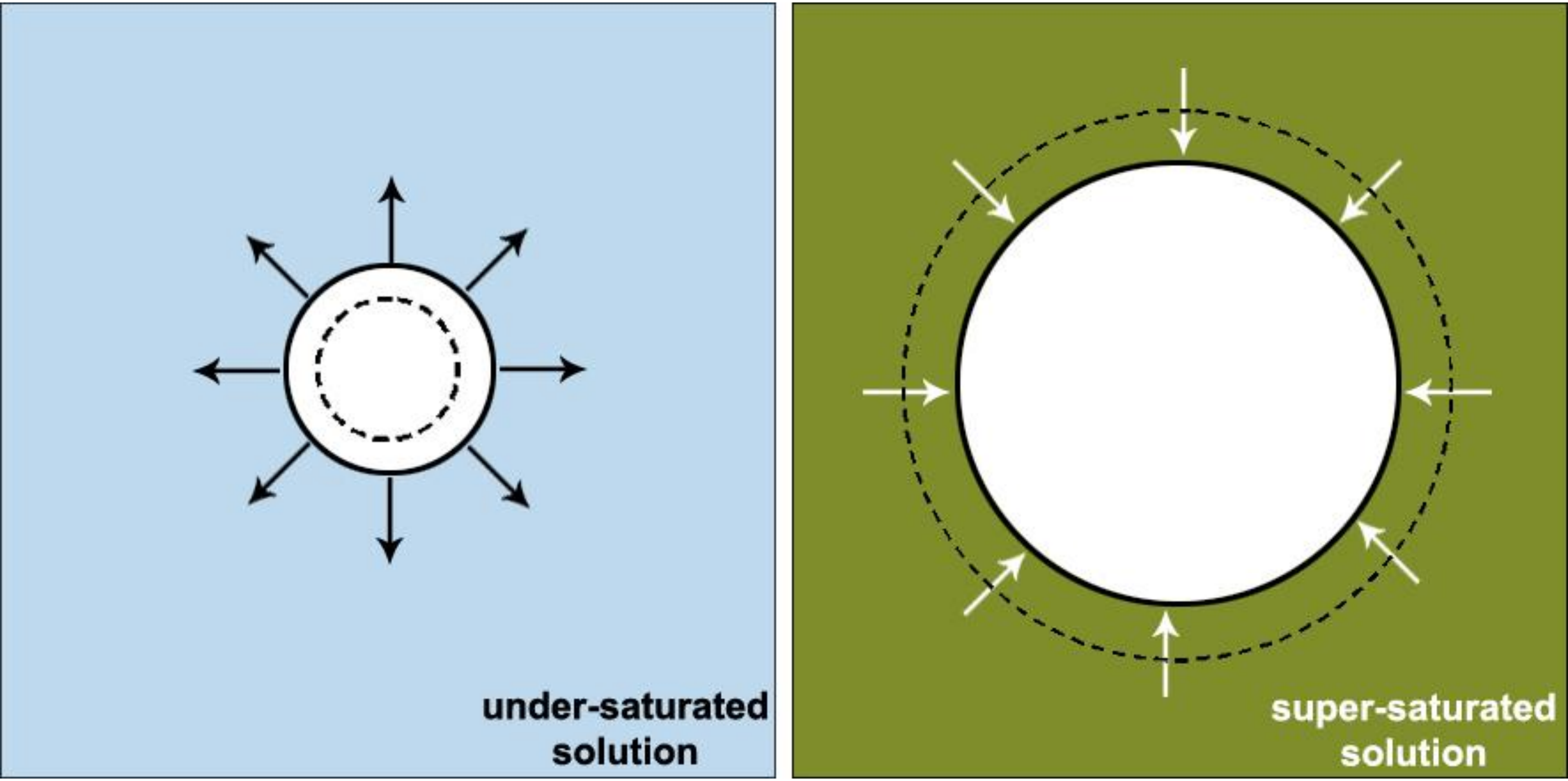
Saturation in the vicinity of a bubble depends on the pressure inside the bubble.

Smaller bubbles have higher internal pressure than larger ones.

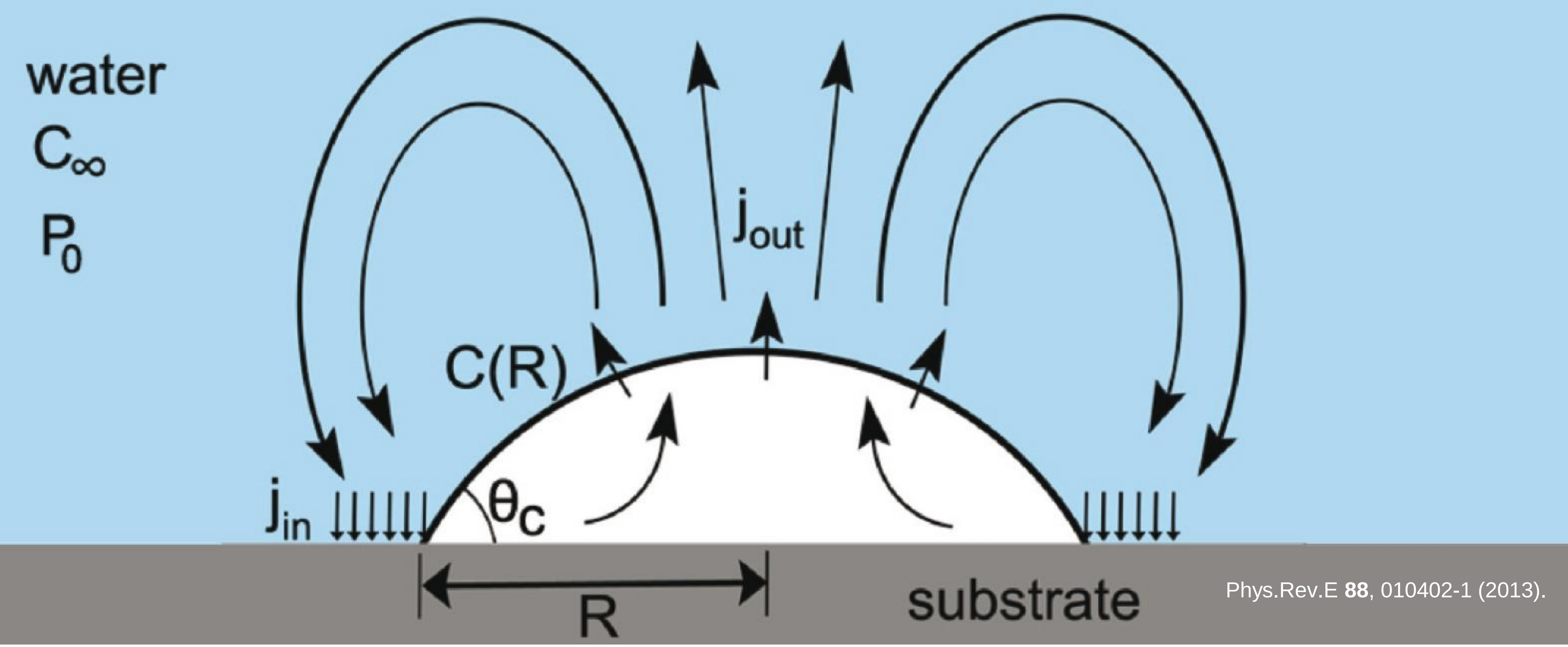
Smaller bubbles release gas to the under-saturated solution.

Larger bubbles grow by taking up gas from super-saturated solution.

Thus small bubbles shrink and large bubbles grow.



Stability of SNB



Phys.Rev.E **88**, 010402-1 (2013).

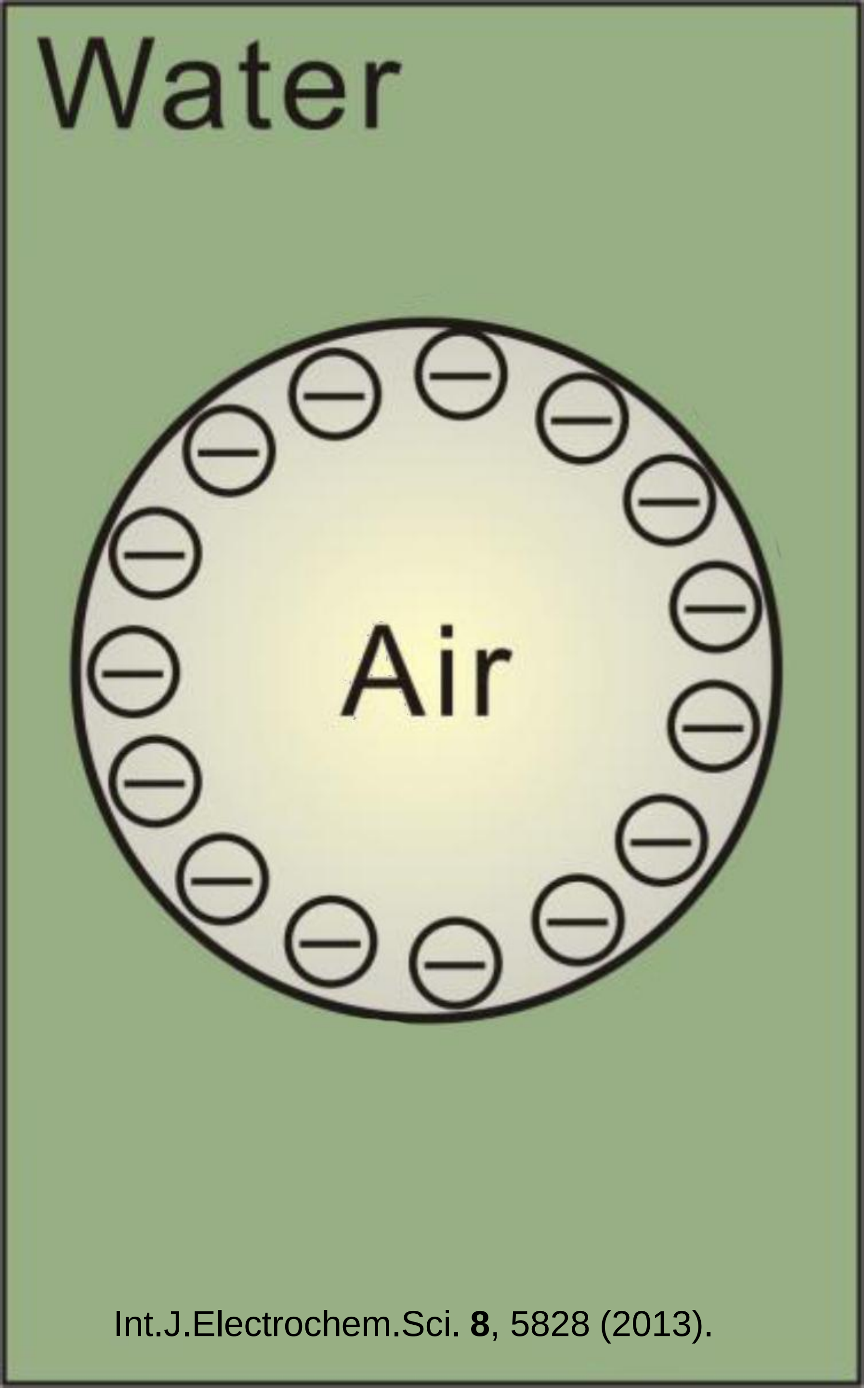
$$j_{out} = \pi RD\left[1 - \frac{C_\infty}{C(R)}\right]$$

$$j_{in} \approx \frac{2\pi sDR}{\tan\theta_c}$$

Where:

j is the volume flux rate out or in. D is the diffusion constant. R is the bubble radius. C_∞ is the gas concentration far away. C(R) is the concentration of the gas at the bubble surface. s is the wall attraction strength. θc is the contact angle.

M.P.Brenner and D.Lohse; Phys.Rev.Lett. **101**, 214505 (2008).



Int.J.Electrochem.Sci. **8**, 5828 (2013).

Stability of BNB

Nanobubbles have a gas/liquid interface of negative charge that introduces an opposing force to the surface tension, preventing their dissipation.

$$\Delta P = \frac{2\sigma}{R} - \frac{\varepsilon\zeta^2}{R^2}$$

Where:

ΔP is the pressure difference.

R is the radius of the bubble.

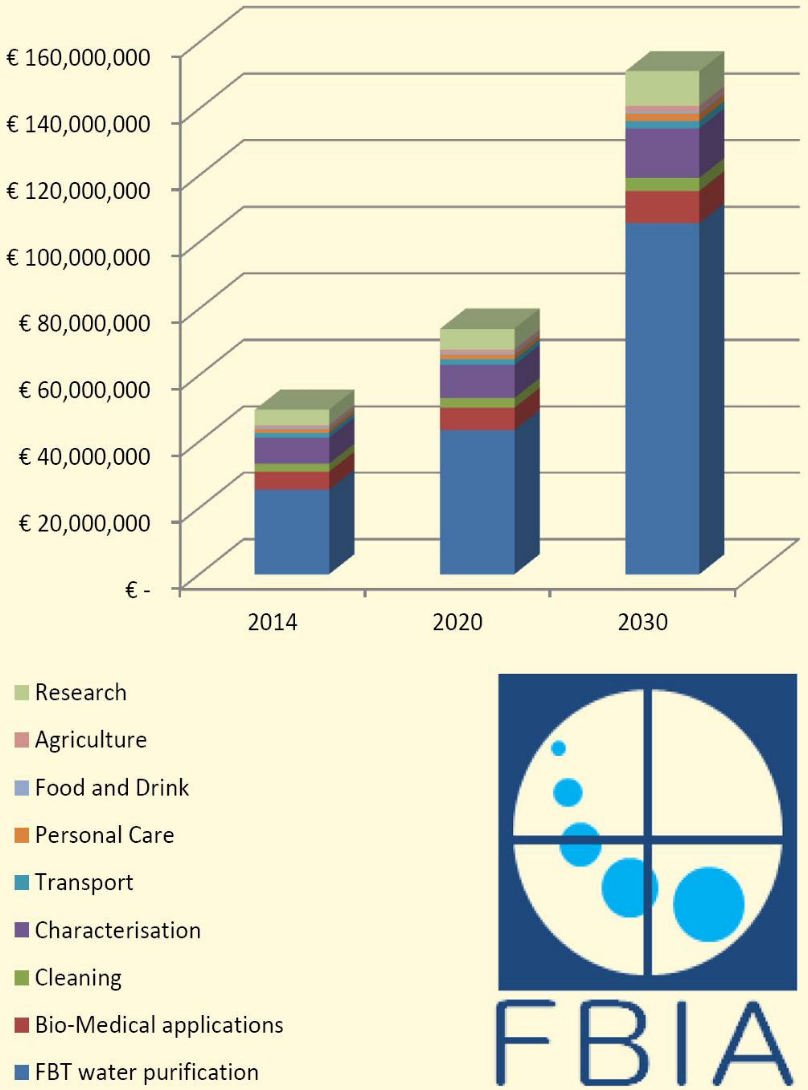
ζ is the zeta potential.

ε is the electric constant.

The last term of the equation is the repulsive pressure of the electrostatic force due to the charged surface of a bubble.

K.Yasui et al.; Ultrasonics Sonochemistry **48**, 259 (2018).

Nanobubble market



FBIA

Nanobubbles are used in many industrial and biological processes such as: water cleaning treatment, flotation, food industry, acceleration of metabolism, intracellular drug delivery, ultrasonography, etc.

The Fine Bubble Industries Association (FBIA) shows a business growth from:

$20 million 2010 to $4.5 billion 2020.

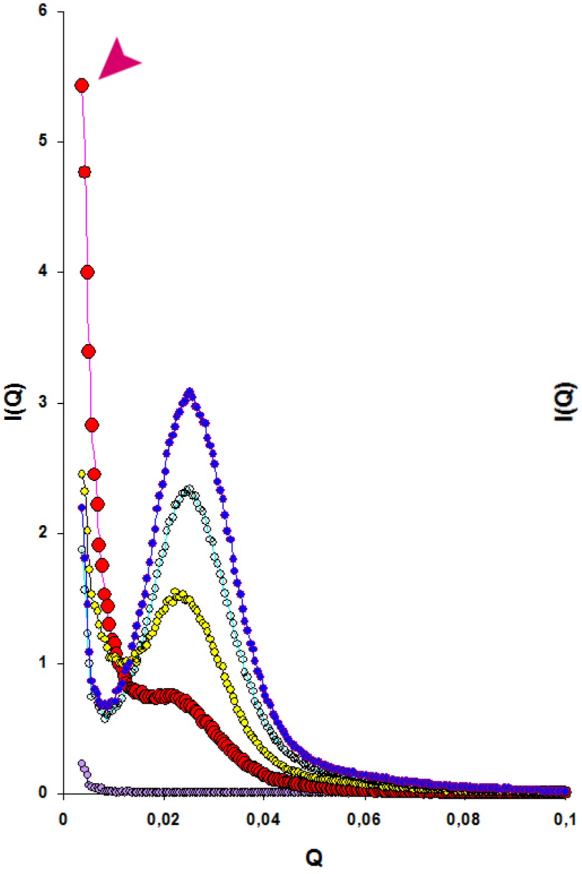
In EU, business is expected to grow from:

€72 million 2020 to €145 million 2030.

The EU market for fine bubble technology was found to be dominated by the water treatment sector with over 52% of the total. Biomedical, research and characterization areas of activity are most promising after the water treatment.

D.K. Koltsov, Fine bubble technology in EU, BREC Solutions Ltd (2016).

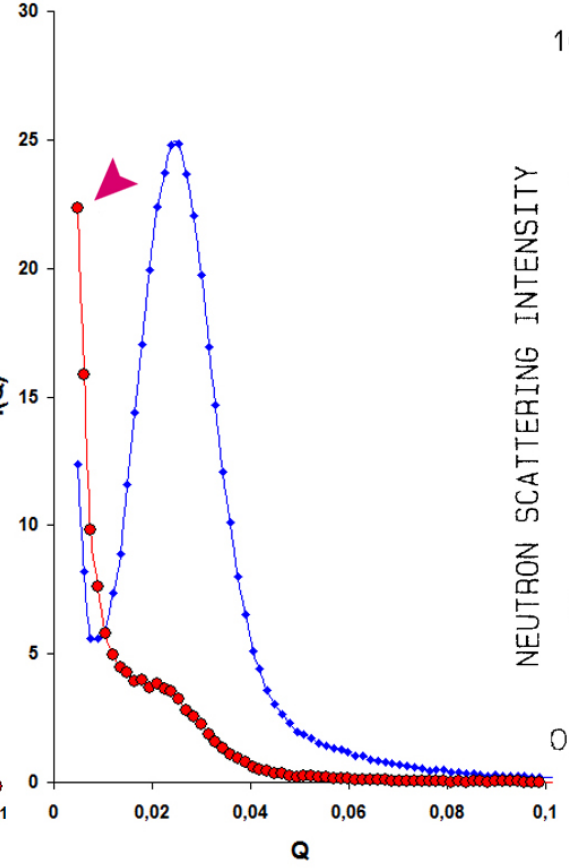
2015



Kavala

Sci.Rep. **5**, 10943

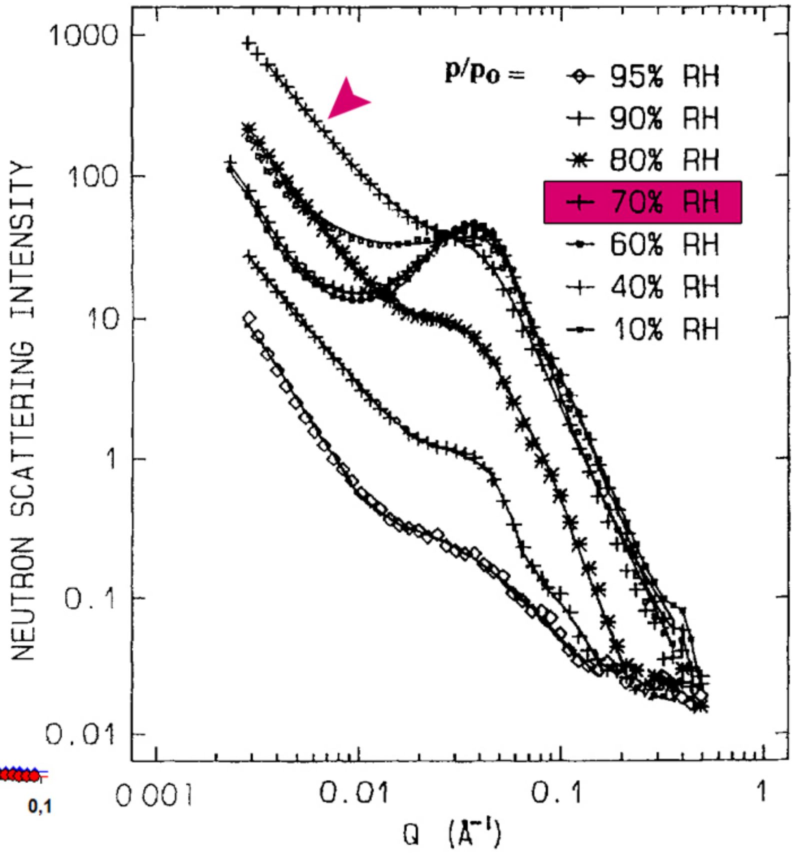
1995



Bristol

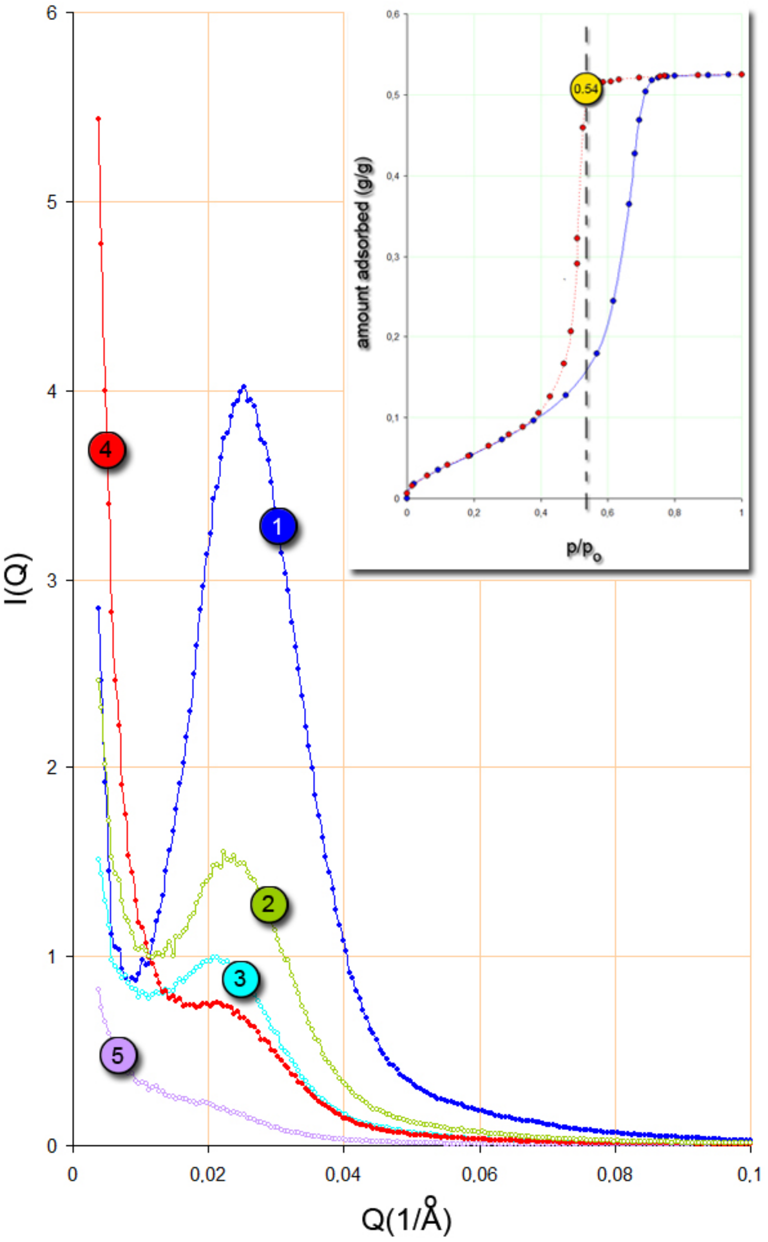
Phys.Rev.B. **52**, 10035

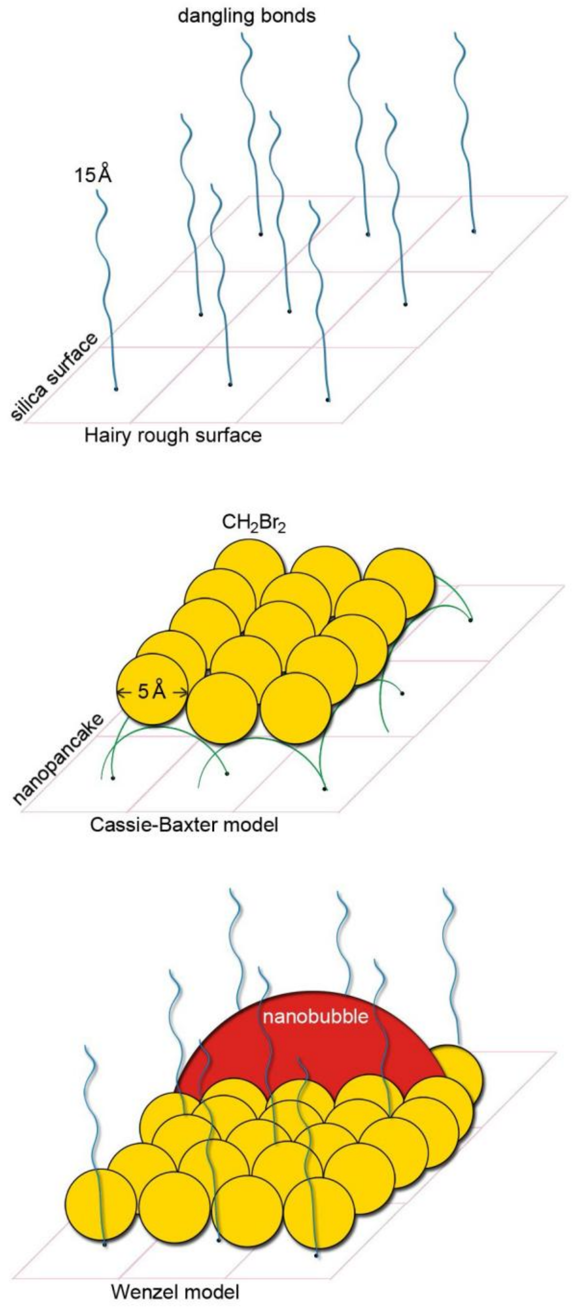
1994



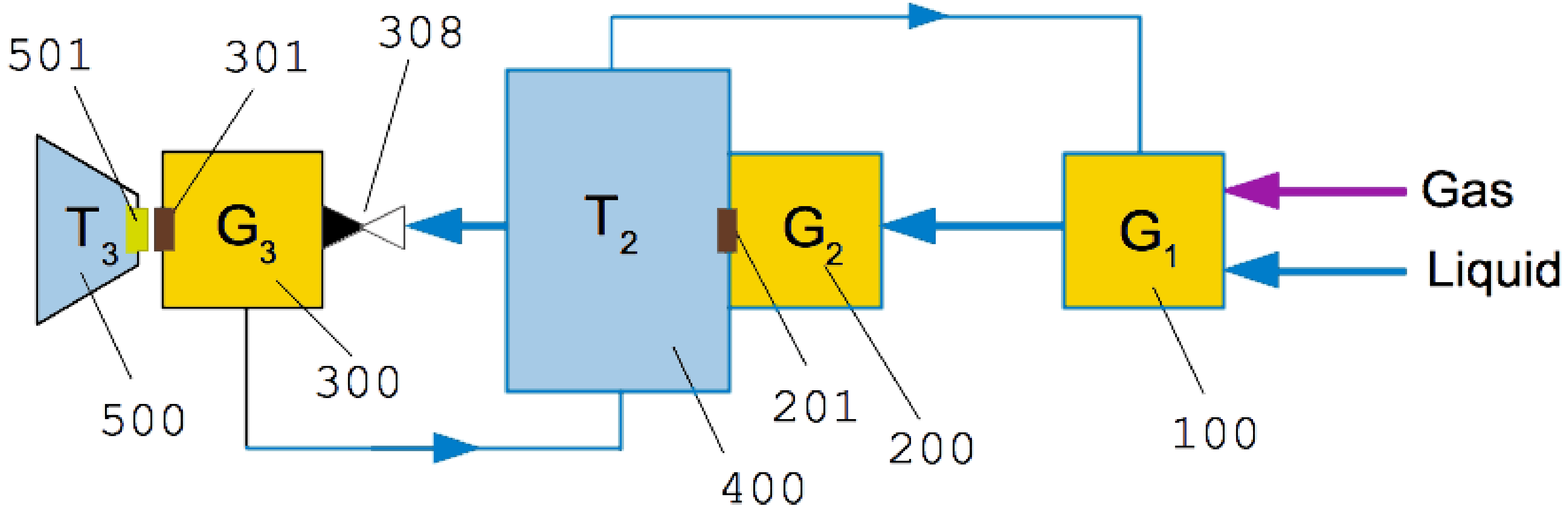
Grenoble

Phys.Rev.B **49**, 5911





Mitropoulos, A.C., Stefanopoulos, K.L., Favvas, E.P., Vansant, E., Hankins, N.P. On the formation of nanobubbles in vycor porous glass during the desorption of halogenated Hydrocarbons (2015) Scientific Reports, 5, art. no. 10943.



Schematic illustration of Nanobubble Generating Device.

i. The system consists of three generators connected in series.
ii. Air and water are introduced to G1 [100] to produce MB.
iii. The MB/water is fed to G2 [200] where it passes through a rotating porous plug [201] generating MNB which in turn are stored in Tank [400].
iv. The MNB/water can be circulated back to G1 or pumped to G3 [300].
v. A check valve [308] prevents the liquid from returning back to G2.
vi. In G3 the liquid is compressed at 150 bar where a porous plug [301] rotates to generate NB.
vii. The NB/water can be collected in Tank 3 [500] or deposited on HOPG [501].

A. Mitropoulos and G. Bomis, Device for generating and handling Nanobubbles: EP2995369 A1/16-3-16.

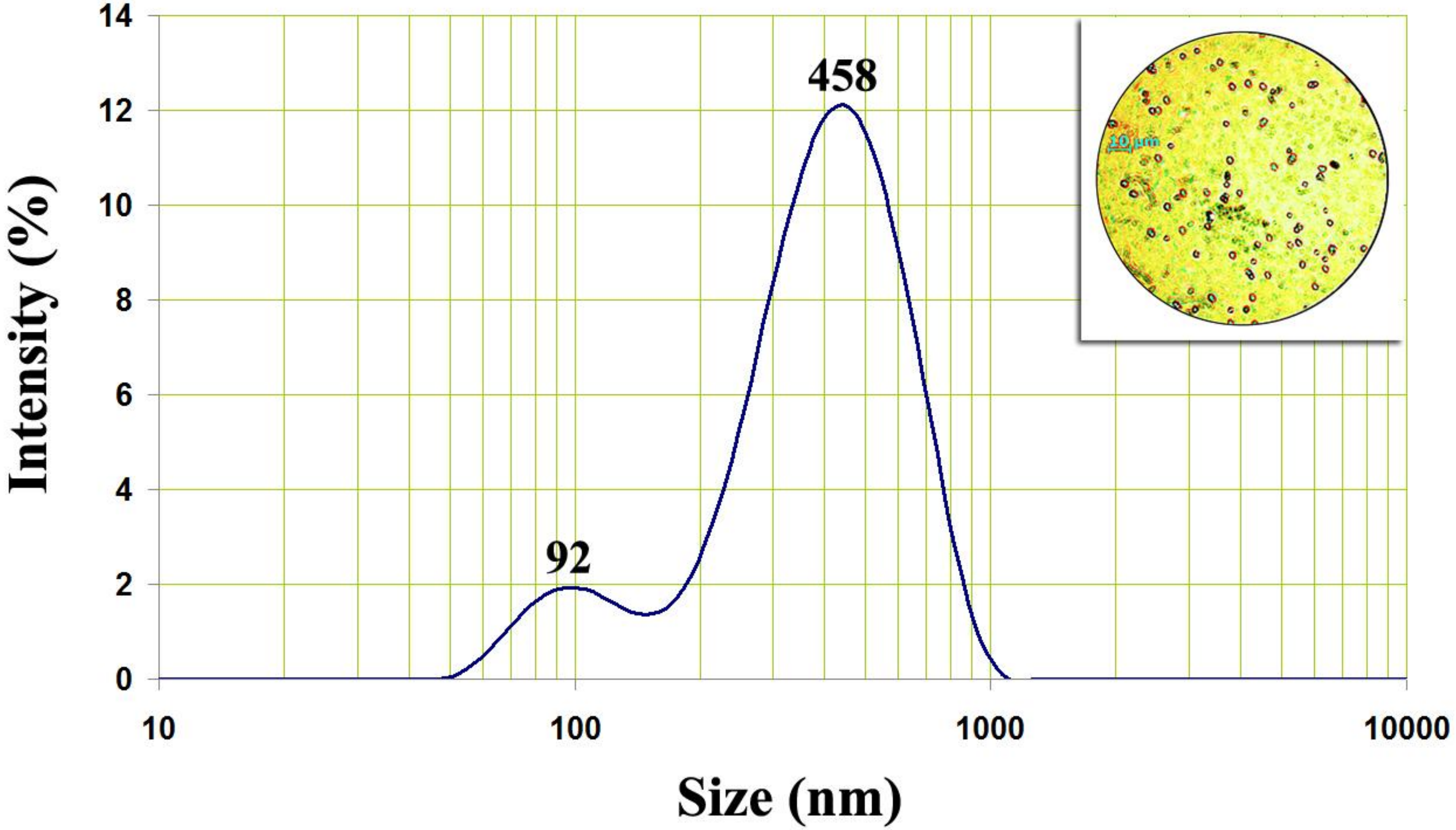
Tyndall Effect

- ✓ As a first evidence of the existence of gas phase in the water, the sample was hit with a green beam laser pointer.

Tyndall Effect was observed!

This observation indicates that the system is ***colloidal,i.e. there is a gas phase dispersed in the water in the form of nanoscopic bubbles !***

Dynamic Light Scattering



Concentration > 850,000 MNB/cm^2 and $\zeta = -8.6$ mV

Synthesis procedure:
From lignite to activated carbon

- ✓ Bench-scale carbonization/activation was conducted with 100g samples that were dried in an oven a 100 °C under N2.
- ✓ The coal was heated to 400 °C in a tube furnace (6 h).
- ✓ The char was then heated in the tube to 750 °C and N2 was passed through the char for activation.
- ✓ Yields of activated carbon were generally about 35-40%.

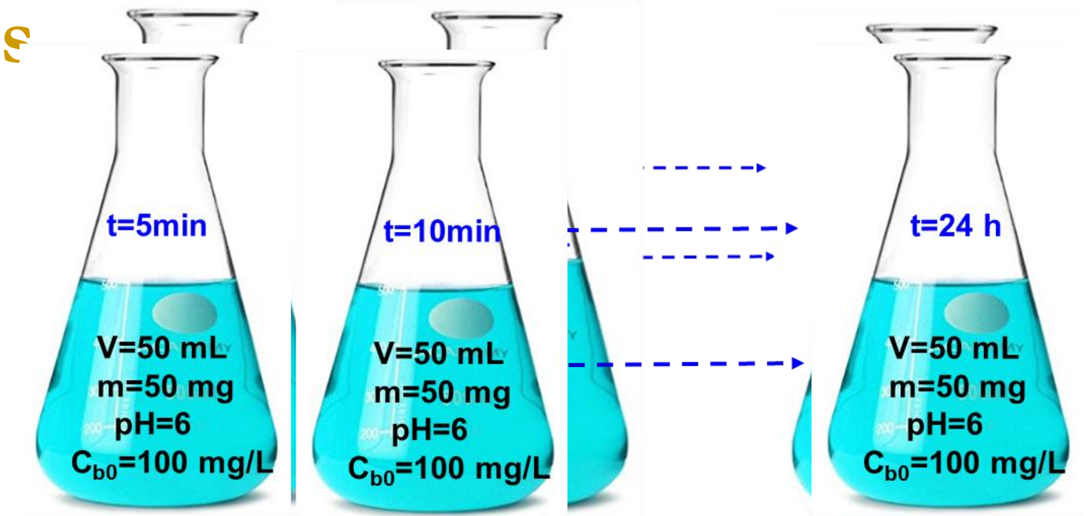
Experimental procedure steps

1. Aqueous Pb(II) solution was prepared by using $Pb(NO_3)_2$ (of p.a.≥99.0%).
2. The pH of the solution was kept to pH=6.
3. The pH was adjusted with micro-additions of HNO_3 or NaOH (0.1 M).
4. For adsorption isotherms the following conditions were applied:
    - i 50 mg of AC per 50 mL of adsorbate solution.
    - ii various initial ion concentrations C_{b0} = 10 to 300 mg/L.
    - iii agitation rate N=150 rpm
    - iv isothermal temperatures at 25, 45, and 65 °C.
5. The experiment was carried out with and without NB.
6. For adsorption kinetic the following conditions were applied:
    - i pH=6; N=150 rpm; m=50 mg; V=50 mL, and T=25°C.
    - ii C_{b0}=100 mg/L.
    - iii time-intervals of 5 min for 24 h.
7. After adsorption, the Pb(II) ions were quantitatively analyzed by atomic absorption spectrometer.

Adsorption kinetics

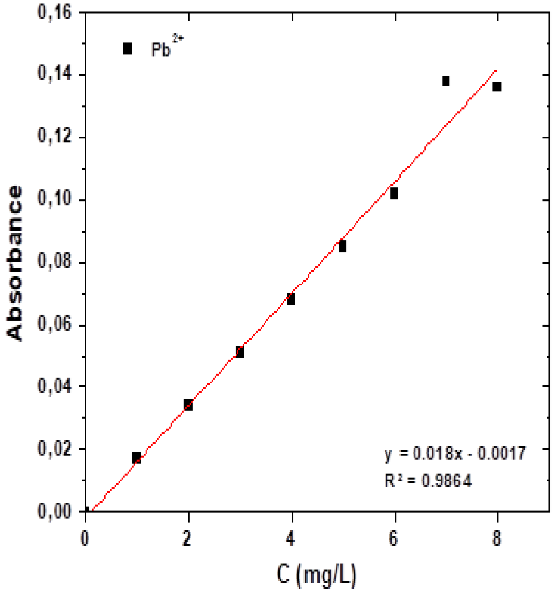
isotherms

1. Preparation of solutions (flasks)



2. Add the flasks in shaking bath at 25 °C, N=150 rpm

3. Atomic Absorption



4. Calculation of bulk solute concentration Cb

Adsorption dynamics

The rate of concentration change dq/dt is given as:

$$\frac{dq}{dt} = k\left(q - q_e\right)$$

$$q_e = \frac{Q_{max} \cdot b \cdot C_b}{1 + b \cdot C_b}$$

$$C_b = C_{b0} - \frac{m}{V} q$$

Where:

q=[adsorbed weight] / [adsorbent weight]

qe is the equilibrium adsorbed quantity that correspond to the instantaneous bulk solute concentration Cb.

Cb0 is the initial bulk solute concentration.

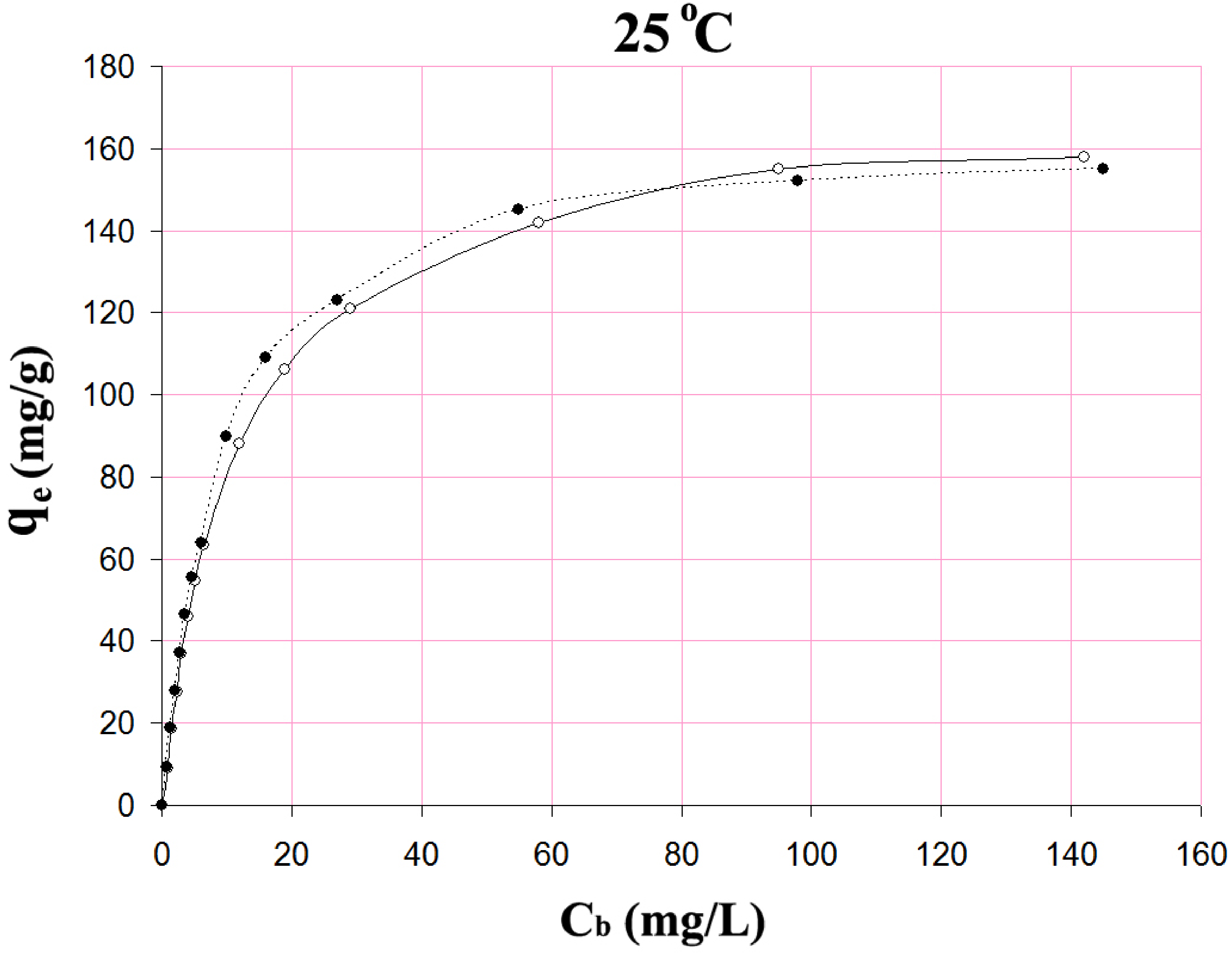
m is the mass of the adsorbent.

V is the volume of adsorbate solution.

At 25oC

With NB: Qmax=171,2mg/g and b=0.087L/mg

Without NB: Qmax=167 mg/g and b =0.108 L/mg



25 °C
q_e (mg/g)
C_b (mg/L)
0
20
40
60
80
100
120
140
160
180
0
20
40
60
80
100
120
140
160

Adsorption kinetics

$$k = \frac{k_0}{1 + \lambda q^n}$$

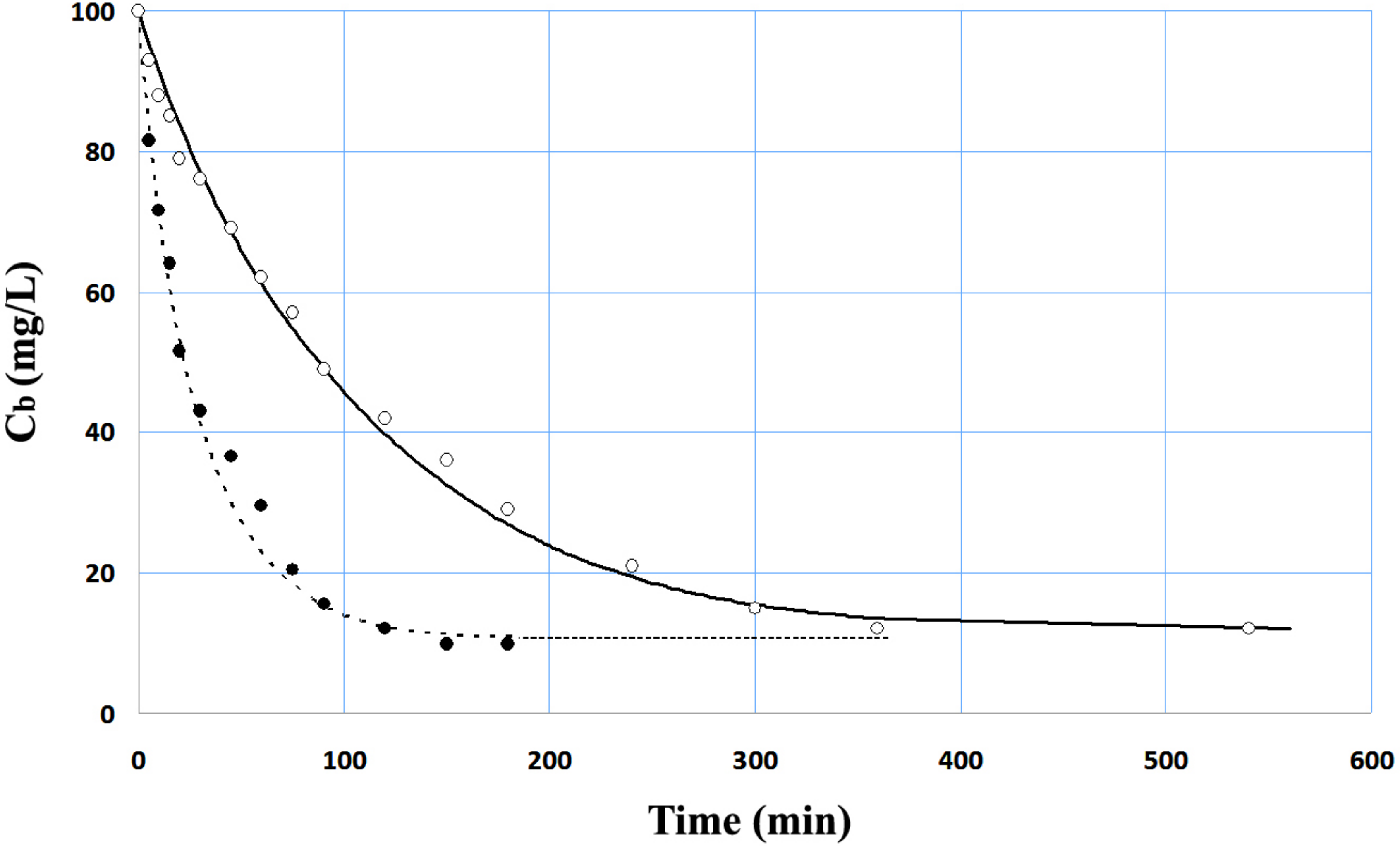
Where:
k is the surface diffusion coefficient.

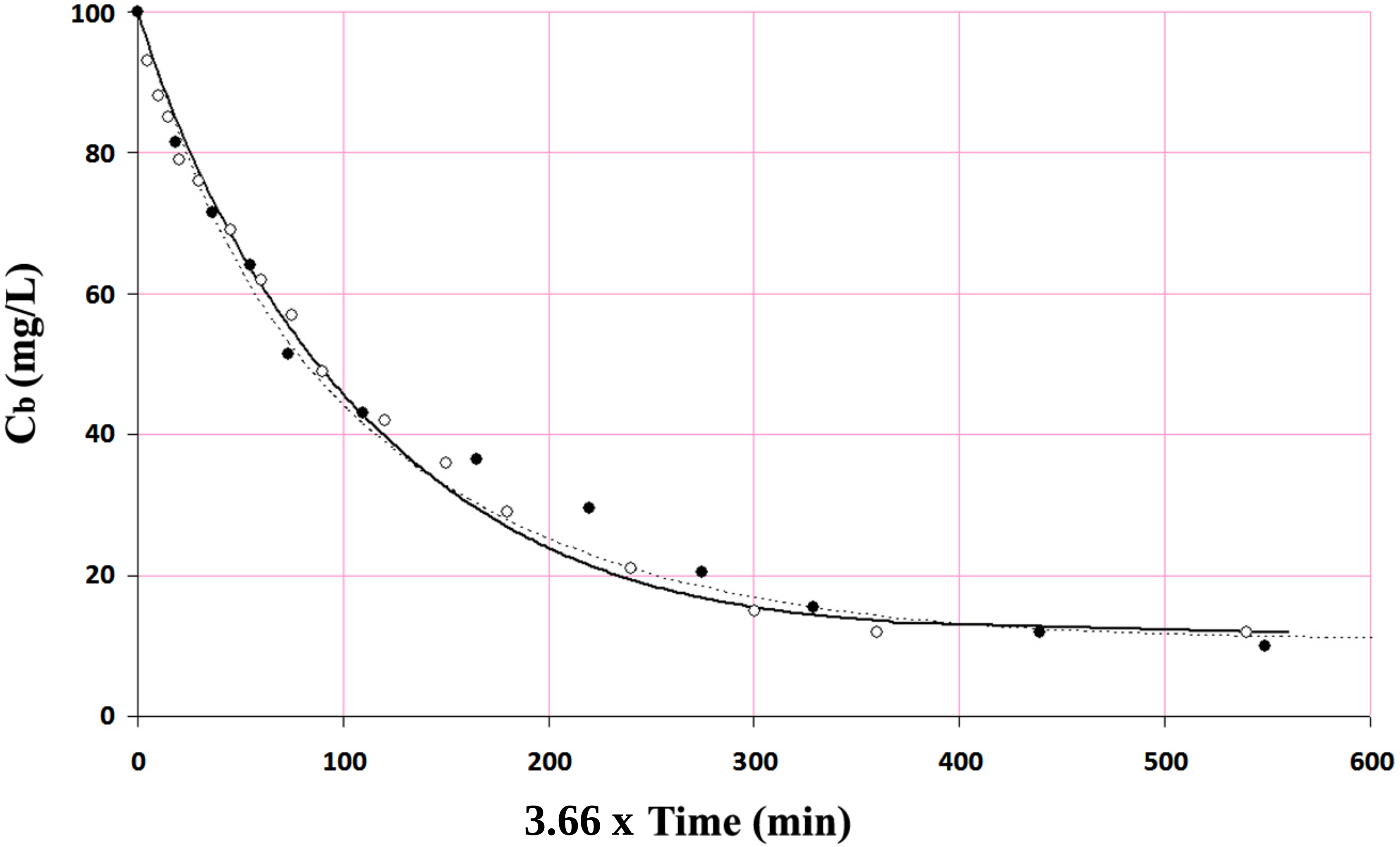
The fitting parameters
With NB: k0=0.006 min-1, λ=0.01 g/mg, n=1.
Without NB: k0 =0.22 min-1, λ=0.00025 g/mg, n=2.

The comparison between fitted curves and experimental data is presented in the next Figure.

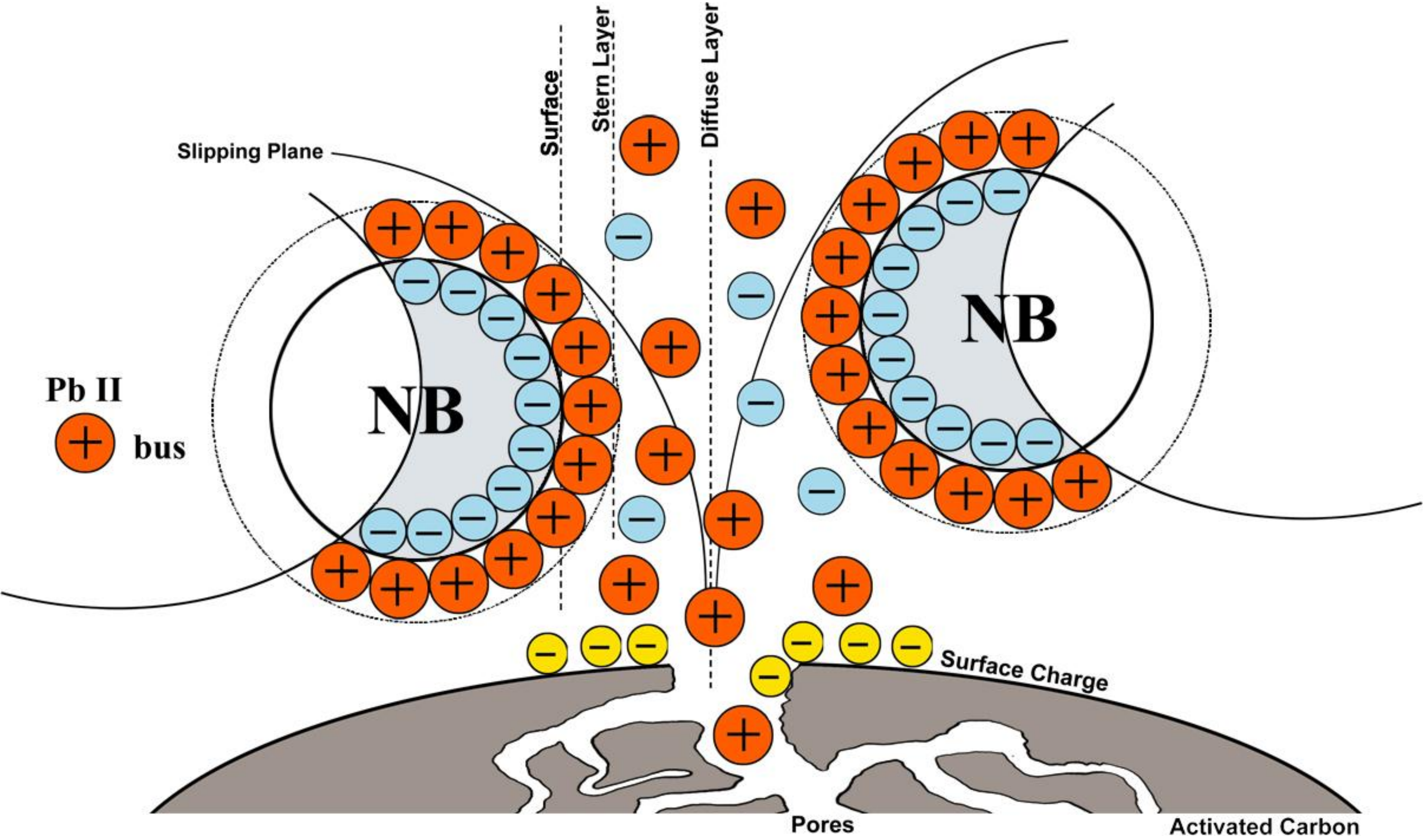
The model describes very well the data in the absence of NB.

The fitting quality is not so high in the presence of NBs, indicating that the mechanism is more complex than simple surface diffusion.


100
80
60
40
20
0
0
100
200
300
400
500
600
C_b (mg/L)
Time (min)


Cb (mg/L)
100
80
60
40
20
0
0
100
200
300
400
500
600
3.66 x Time (min)

Mechanism



G.Z.Kyzas, G.Bomis, R.I.Kosheleva, E.K.Efthimiadou, E.P.Favvas, M.Kostoglou, A.C.Mitropoulos; Chem.Eng.J. **356**, 91 (2019).

Activated carbon and then graphene from lignite

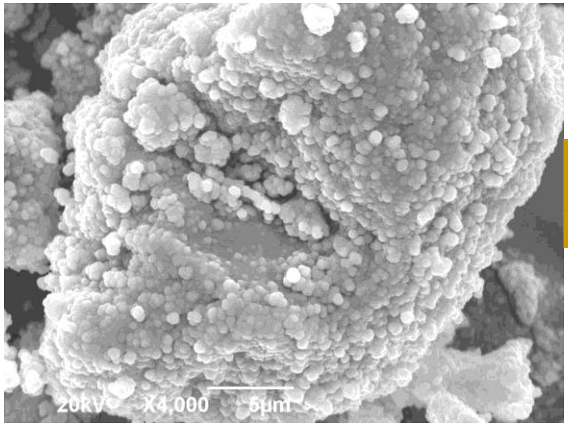
The process is based on the conversion of lignite to humic acid and subsequently to graphene oxide prior to preparation of the final product (graphene).

Six steps:

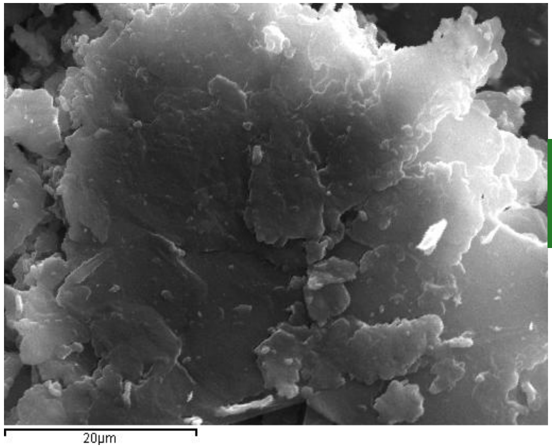
1. Conversion of lignite to carbon.
2. Activation of carbon to activated carbon.
3. Conversion of activated carbon to graphite.
4. Conversion of graphite to graphite oxide.
5. Conversion of oxide of graphite to graphene oxide.
6. Reduction of graphene oxide to graphene.

The finished product is of high purity graphene (77%) from lignite (zero purchase cost).

Activated carbon and then graphene from lignite



Graphene oxide



Graphene [77% purity]

To be patented under the financial support of project: “Development of NAnotechnology-enabled “next-generation” MEmbranes and their applications in Low-Energy, zero liquid discharge Desalination membrane systems”/NAMED, T2ΔΓΕ-0597.

Thank you for your attention

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