Bioremediation using packed bed bioreactor technology in mercury-containing wastewater.

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Introduction and objectives

The presence of mercury in the environment is increasing over the years. Industrial activities are the main responsible for mercury emissions, that's why bioremediation technologies have to be designed and microorganisms seem to be a promising tool for it.

The aim of this work is:

-Know general aspects of mercury: cycle, impact on human health, uses, contamination sources…

- Study the role of microorganisms in this problematic and their molecular mechanism.

- Know the basis of packed-bed bioreactor system and main results reported using this technology.

Mercury in the environment

Mercury is a natural component of the Earth mantle and it is classified as the third most toxic substance. Once mobilized in the environment it's difficult to control. This metal can cycle through land, air and water (see *figure 1*), undergoing a number of complex chemical and physical trans-formations. Once mercury is present in a biological system, it can bioaccumulate. As a consequence, affections inneurodevelopment, damage to the cardiovascular system, kidney and bones occur.

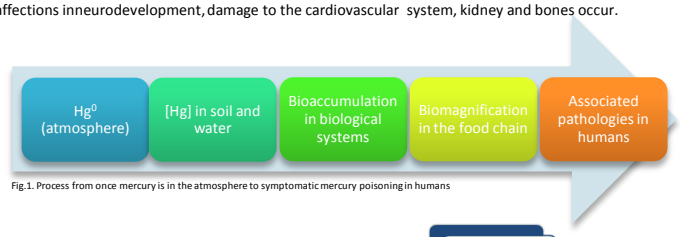

Fig.1. Process from once mercury is in the atmosphere to symptomatic mercury poisoning in humans

Mercury is being used for lots of applications (see *figure 2*) since the industrial era. The concentration of this metal has increased substantially in different ecosystems [1]. Even thought, contamination for natural phenomenon it also exist (Fig.2).

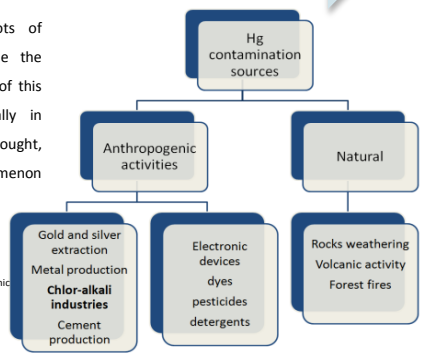

Fig. 2. Natural and anthropogenic Hg contamination sources.

Chlor alkali current situation

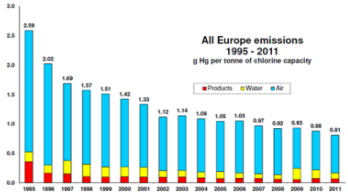

Fig.3. Trend of mercury emissions for all European chlorine producers since 1995 to 2011 [2].

Chlor-alkali industries is one of the main mercury users [3] but new regulations have changed the situation and global mercury emissions by these industries have been reduced (Fig. 3):

- The mercury technology will be phased out in 2020→ Decrease the number of plants.
- Using best environmental technologies.

Removal of mercury from wastewater by microorganisms

In order to fulfill the mercury discharged limit requirements in wastewater (50 µg /L) clean-up technologies have to be implemented in some industries. Biological systems are based on mercury resistant bacteria.

Operon *mer* (mercury resistance, Fig.4)
It encodes for:

- *merA* (Hg reductase)
- *merB* (organomercury lyase)
- *merP* (periplasmic Hg(II) protein)
- *merT, C, E, F, G* (cytoplasm transporter)
- *merR, D* (regulatory proteins)

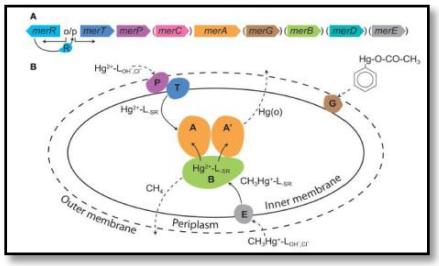

Fig. 4. The *mer* system. (A) A generic *mer* operon with genes in parentheses depicting those that are present in some but not in almost operons. (B) The cellular *mer*-encoded mercury detoxification mechanisms [4].

The detoxification is done by the reduction of Hg(II)-compounds to metallic mercury which is less toxic for microbial life (see *figure 5*). About 1-10%of cultured heterotrophic aerobic microbes from various environments possess *mer* systems [4].

$$Hg^{2+} + NADPH_2 \xrightarrow{merA} Hg^0 + NADPH + 2H^+$$

Fig.5 . The one-step mercury detoxification reaction by merA.

Packed-bed bioreactor

It consists of a carrier material covered by a biofilm of mercury-resistant bacteria. It has to be completely submersed in a liquid phase to avoid Hg^0 diffusion. The less soluble elemental mercury collects in the the microbial mass as small droplets (see *Figure 6*) which must be subsequently extracted using another technology [5].

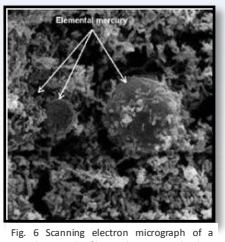

Fig. 6 Scanning electron micrograph of a *Pseudomonas* biofilm and mercury droplets (arrows) [5].

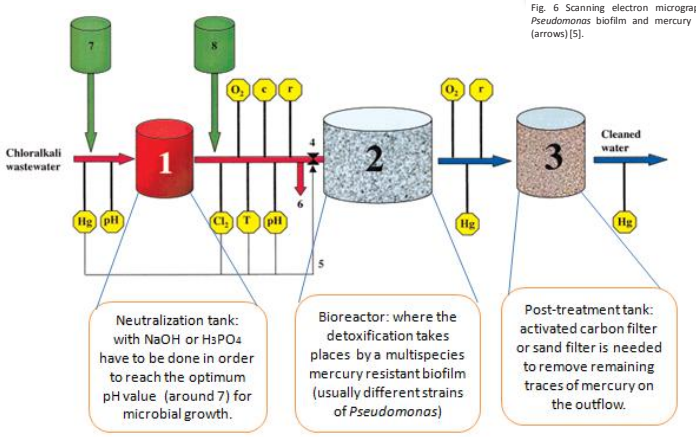

Fig. 7. Scheme of pilot plant for microbial mercury remediation. Numbers refer to tanks or valves, yellow octagons to monitors. 1 neutralization tank; 2 bioreactor; 3 activated carbon filter, 4 bioreactor inflow valve; 5 control of bioreactor inflow valve; 6 bypass; 7 sodium hydroxide tank; 8 medium tank; Hg automated continuous mercury measurement; oxygen conductivity, chlorine pH pH redox potential and temperature probes. [6]

After *Pseudomonas* inoculation some days are needed to form the biofilm (Fig. 8). However, some successions can occur [6].

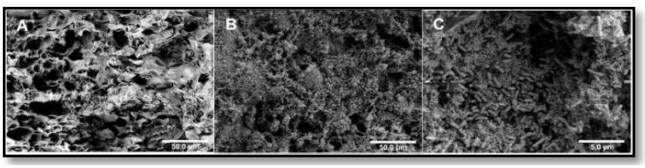

Fig. 8. Biofilm evolution. Scanning electron micrograph. (A) After 2 days of operation,. (B) After 224 days of operation, a dense biofilm covered the surface. (C) The 224-day-old biofilm consisted of rod-shaped *Pseudomonas* cells embedded in a thick layer of EPSs [6].

Results and conclusions

Clean-up technologies are need to bioremediate mercury wastewater. Pilot plants using packed bed bioreactors have been implemented in few factories in order to reduce mercury load in their wastewater. They were successfully operated in technical s been observed (Fig. 9) even its limitations [4,5].

- Efficiency: 90-98%
- [Hg] inflow=3-10 mg/L
- [Hg] outflow= less than 50 µg Hg/L
- [Hg] ACF= less than 10 µg Hg/L

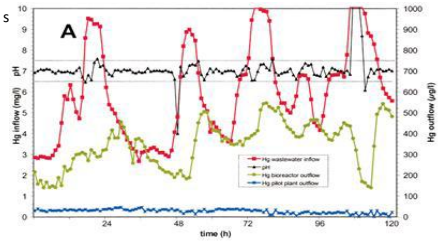

Fig. 9. Wastewater fluctuations. [Hg] in the wastewater, in the bioreactor effluent, and in the activated carbon filter effluent. The pH of the wastewater after neutralization.[6]

Even chlor-alkali industries (based on Hg process) will be pashed out, this system can be used in other types of mercury contaminated wastewater.

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