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A Flow-By Reaction System for Removing Heavy Metals From a Biological Process Stream

Série Tecnologia Ambiental

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PRESENTATION

This preliminary study, produced by the Researcher Dr. Luiz Sobral, approaches an up to date theme, i.e. the effluents heavy metal recovery.

In his experimental approach, the author studies the withdrawal of Cd^{2+}, Zn^{2+} and Cu^{2+} from solution simultaineously containing the three ions by using a tridimensional electrode with expanded area, also investigatin the possibility of the selective recovery of the three metals.

The approach, as well as the methodology of the study and its promising results will be of great use for those interested in this matter.

Rio de Janeiro, December, 1999.

Fernando A. Freitas Lins
Director

C O N T E N T S

RESUMO

Neste estudo foi examinada a remoção de zinco, cádmio e cobre, de uma solução aquosa em meio sulfato, derivada do processo de desorção desses metais da biomassa, usando um sistema reacional com um eletrodo tridimensional com área superficial expandida (RNiF). Esse sistema foi considerado como sendo extremamente efetivo na redução das concentrações dos metais supracitados para a faixa de ppb. Foi estudado o efeito do potencial catódico e a vazão de eletrólito através de esponjas metálicas de níquel em três porosidades distintas. Além disso, foram registradas curvas corrente potencial, utilizando-se um eletrodo de rotatório de carbono vítreo, visando averiguar a possibilidade de depositar os metais acima mencionados separadamente.

Palavras-chave: *Eletrodo tridimensional, metais pesados*

ABSTRACT

In this study the removal of zinc, cadmium and copper, from an aqueous sulphate solution, derived from the biomass desorption process, was examined by using a reaction system with a three-dimensional high surface area electrode (RNiF). This reaction system was found to be extremely effective in reducing metal concentrations to the ppb range. The effect of cathode potential and flow rate were studied for three different nickel foam porosities. In addition, current-potential curves were recorded, at a rotating vitreous carbon electrode, to determine the possibility of depositing the aforementioned metals separately.

Keywords: *Three-dimensional electrode, heavy metals*

1. INTRODUCTION

In recent years public awareness has increased as the long term toxic effects of water containing dissolved metal ions. Numerous industrial processes produce aqueous effluents containing heavy metal contaminants. These pollutant concentrations must be reduced, to meet ever increasing legislative standards; metal must be recovered where feasible. Consequently improved and innovative methods of wastewater treatment are continuously being developed to deal with effluents containing dissolved waste metals which may not be treated by conventional processes.

Restrictive environmental legislation, ecological problems due to dispersion of heavy metals in natural environments, and the high cost of technologies for treating effluents containing heavy metals have stimulated the development of technologies to compete with/or complement conventional techniques. Among the technologies under development, much is being written about techniques involving the use of micro-organisms (bacteria, fungi and micro algae), and, above all, inactivated seaweeds. Several examples have proved the potential use of micro-organisms to accumulate heavy metals; but the results, however, are still away from a technological reality that could render the use of micro-organisms technically and economically viable as biological metal adsorbents. Nevertheless, employing of other biological materials, such as plants and seaweeds, allows us to apply the knowledge available from conventional processes to develop a technology for treating heavy metals bearing effluents.

The competitiveness of a new technology for heavy metals recovery depends upon a series of factors related to the characteristics of the biomass as well as to the operational system. One such viable system would employ fixed-bed reactors such as conventional processes that use ion-exchange resins or activated carbon. This type of system permits treating great volumes of solution, although limited by the loading of the

biomass by heavy metals. At this stage, desorption of metals is necessary for reusing the biomass in successive sorption/ desorption cycles.

Toxic metals are usually present at high concentrations in several kinds of effluents, especially those from metallurgical activities. According to their high toxicity, it is of great interest to develop a recovery process which may prevent their discharge into water streams.

The intensification of industrial activities during the last few years, is greatly contributing to an increasing dispersion of toxic compounds in natural environments, mainly in aquatic systems. In most cases, it is possible to reduce dramatically the level of toxic substances through the use of conventional technologies, although the cost associated to these processes is very high and the efficiency of the treatment not fully satisfied. When these compounds are associated to metals ions those technologies are not completely efficient, and the non-degradable nature of these elements, dictates that they must have suffered additional treatments to fulfil the new environmental directives.

The remarkable ability of biomasses to concentrate heavy metals, acting as a biological resins, is becoming an useful tool for treating industrial solutions contaminated with heavy metals. This phenomenon, generally called biosorption, is easily handled by using one of those conventional fixed-bed reactors designs. This reactor usually has a very simple operational mode, with a reduced cost, in comparison to sophisticated treatment techniques. So, the biosorption should be used as a complementary technology to treat effluents contaminated with heavy metals.

For the effective implementation of a biosorption technology for the accumulation of heavy metals, a series of conditions should be considered:

(i) the biomass should accumulate around 100 mg metal/g biomass; *(ii)* biosorption and desorption should be rapid and efficient; *(iii)* the biological material must be cheap and reusable, and, *(iv)* the biological material should be adaptable to different reactors.

After saturation of the biomass with the heavy metals, an elution should be made, in order to regenerate the biomass for further use, with the production of highly concentrated solution, feasible for recovering the heavy metals. The regenerated biomass returns to the adsorption process.

Electrodeposition is an important and effective method for the recovery of and recycling of metals from, mainly aqueous, process streams. The range of implications is diverse with several commercial cell designs available[1]. Although many waste and process solutions contain mixtures of metal ions the majority of experimental studies have considered solutions containing single metal ions. Only few have considered aspects of electrodeposition of a single metal ion from a mixture of two metal ions in solution[2-6] .

The effectiveness of electrodeposition in these circumstances depends on a number of factors, such as: relative concentration of metal ions, solution pH and operating temperature, standard electrode potential, kinetics and operating potential, the presence of complexing or chelating agents and mass transport. This effectiveness is measured in terms of current efficiency and energy consumption, space time yield (or operating current density) degree of removal of the relevant metal ion and purity of metal electrodeposited [7].

The nature of electrodeposition frequently requires batch operation, except where continuous metal powder production can be achieved in for example rotating cylinder electrodes[8]. This procedure usually requires operation at the mass transport limiting current density which with mixed metal ion solutions leads to limitations in effectiveness.

This preliminary study reports the removal of low concentrations of Zn, Cu and Cd from a stream being generated during the desorption process of a brown seaweed previously charged with those metals.

2. EXPERIMENTAL

The solution used for deposition of the aforementioned metals contained 0.5 mol dm^{-3} K_2SO_4 (AnalaR) as a base electrolyte and the pH being adjusted to 2 by using sulphuric acid. The metal were introduced into solution by using a stock solution of each one of those prepared dissolving the sulphate salts in water. Solutions were made up using deionized water and de-aerated with oxygen-free nitrogen prior to the electrochemical experiments.

The deposition of metals were studied at a rotating vitreous carbon (RVC) disk (area = 3.7 x 10^{-3} dm^2) embedded in a Teflon® holder and attached to a rotating disk assembly. The RVC electrode was polished to a mirror finish with alumina powder (2-5 μm particle size) just before recording steady-state seep curves. A conventional Pyrex® cell assemble (Figure 1) was used, incorporating a saturated calomel reference electrode separated from the bulk solution by a Luggin capillary; a large platinum foil (4 x 4 cm) in a separate compartment served as a counter electrode.
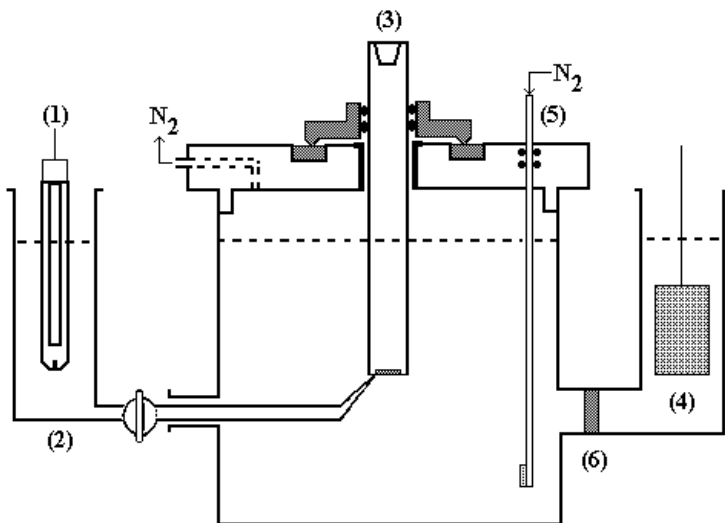
Figure 1 - Experimental cell design for experiments with rotating disk electrode: (1) reference electrode, (2) Luggin capillary, (3) rotating vitreous carbon electrode, (4) platinum foil electrode, (5) nitrogen bubbler, (6) porous glass sinter

The electrowinning reactor system (laboratory cell and flow system) is sketched in Fig.2. The anode used was a platinized titanium mesh electrode and the current collector for the nickel foam cathode was a gold plated copper sheet. The nickel foams used were supplied by Sumitomo Electric Industries Ltd. with 17, 25 and 35 pores per inch (p.p.i.) with respective specific surface areas of 1000, 1700 and 2500 m^{-1}. The anolyte and catholyte were separated by a Nafion$^®$ 417 cation exchange membrane (DuPont). The anolyte and catholyte reservoirs were filled with 4 dm^3 of electrolyte. Both reservoir were fitted with nitrogen bubblers to remove dissolved oxygen. With the exception of the glass reservoirs, the electrolyte flow system was entirely constructed from PVC pipework.
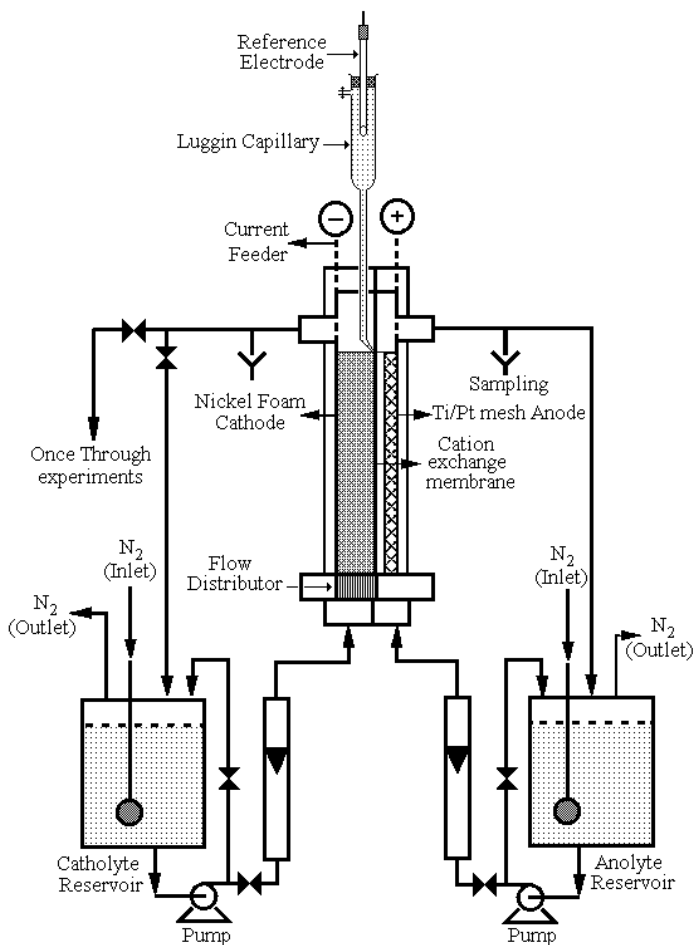
Figure 2 - Reactor system (electrowinning cell and solution flow)

The electrolytes were prepared with deionized distilled water and AnalaR reagents. The anolyte was 0.5 mol dm^{-3} sodium hydroxide plus a mixture of 0.125 mol dm^{-3} $K_4Fe(CN)_6$ and 0.0025 mol dm^{-3} $K_3Fe(CN)_6$. The anodic process was thus the oxidation of potassium ferrocyanide to ferricyanide, as follows:

$$Fe(CN)_6^{4-} \Leftrightarrow Fe(CN)_6^{3-} + e$$
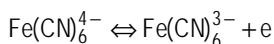
The high ratio of $K_4Fe(CN)_6$:$K_3Fe(CN)_6$ in the anolyte enables oxygen evolution at the anode to be avoided:

$$4OH^- \Leftrightarrow 2H_2O + O_2 + 4e$$
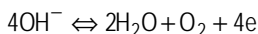
The extent of this subsidiary reaction depends upon process conditions and electrolyte composition.

The catholyte was prepared by using analytical reagents and distilled water. Standard solutions were prepared by dissolving suitable salts of metals in water and/or potassium sulphate which served as supporting electrolyte. The pH of the solution was adjusted with sulphuric acid solution. The concentration of each metal in solution was of 40 ppm (6.3×10^{-4} mol dm^{-3} in Cu^{2+}, 3.5×10^{-4} mol dm^{-3} in Cd^{2+} and 6.1×10^{-4} mol dm^{-3} in Zn^{2+}.

All electrochemical experiments were controlled with a potentiostat (EG&G-Princeton Applied Research, Universal Programmer, model 175). The applied potentials and the resulting currents were stored in a PC computer using data acquisition software (Labtech Notebook) and subsequently analysed. The analysis of metals in the catholyte was carried out by atomic absorption spectroscopy.

3. RESULTS AND DISCUSSION

3.1 Linear Potential Scans with a Rotating Vitreous Carbon Electrode

Figures 3, 4 and 5 illustrate the form of the steady-state polarization curves measured for the cathodic reduction of Cu^{2+}, Cd^{2+} and Zn^{2+} ions at a rotating vitreous carbon electrode.
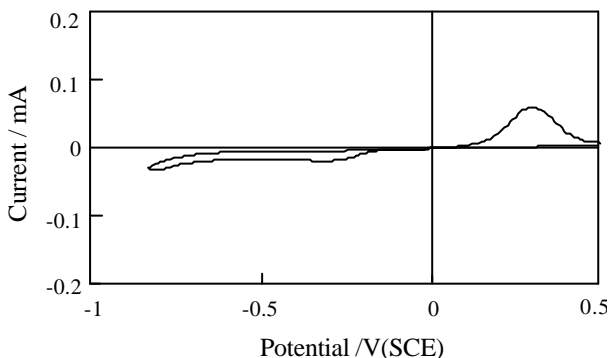

Figure 3 - Steady-state potential sweep profile for the reduction of Cu^{2+} ions. [Cu] = 6.3 x 10^{-4} mol dm^{-3}, [K$_2$SO$_4$] = 0.5 mol dm^{-3}, scan rate = 0.01 V s^{-1} and pH = 2 adjusted with a sulphuric acid solution

The small cathodic peak, in the Figure 3, was thought to belong to the reduction of Cu^{2+} ions which E^o is 0.34 V (SHE). The copper reduction potential for the used Cu^{2+} concentration, according to the Nernst equation, is near to zero V(SCE). During the anodic scan a more distinguished anodic peak which is supposed to be related to the oxidation of copper just deposited.

In the curve of Figure 4 a more distinct reduction peak presumably from the reduction of Cd^{2+} ions, during the cathodic scan. The cadmium reduction potential for the used Cd^{2+} concentration, according to the Nernst equation, is around -0.75 V(SCE). A very distinguished oxidation curve is observed which is supposed to be related to the oxidation of metallic cadmium deposited during the cathodic scan.
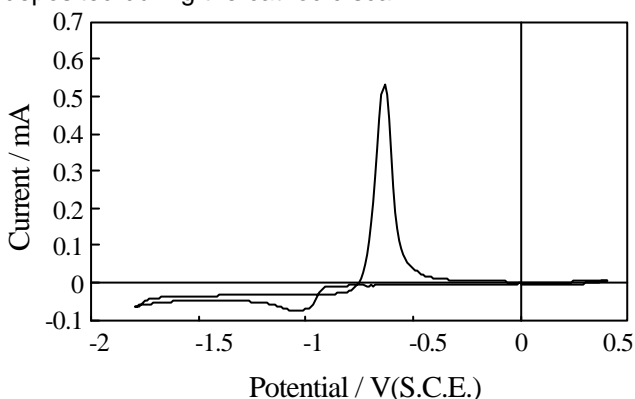

Figure 4 - Steady-state potential sweep profile for the reduction of Cd^{2+} ions. [Cd] = 3.5 x 10^{-4} mol dm^{-3}, [K_2SO_4] = 0.5 mol dm^{-3}, scan rate = 0.01 V s^{-1} and pH = 2 adjusted with a sulphuric acid solution

Observing the curve of Figure 5, it is identified a reduction peak as related to the reduction of Zn^{2+} ions which reduction potential, for the used Zn^{2+} concentration, according to the Nernst equation, is around -1.10 V(SCE).
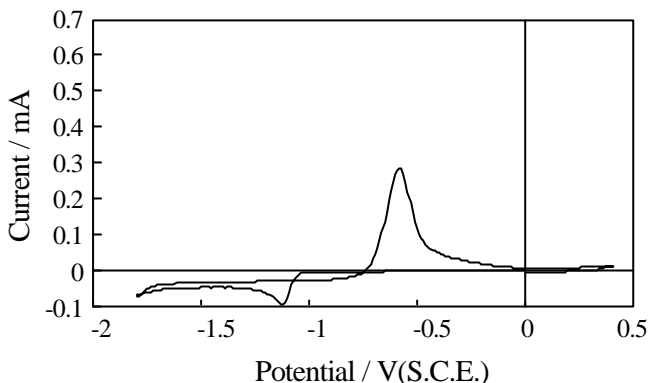
Figure 5 - Steady-state potential sweep profile for the reduction of Zn^{2+} ions. [Zn] = 6.1 x 10^{-4} mol dm^{-3}, [K_2SO_4] = 0.5 mol dm^{-3}, scan rate = 0.01 V s^{-1} and pH = 2 adjusted with a sulphuric acid solution

As above mentioned the reduction potentials of the ions considered in this study (Cu^{2+}, Cd^{2+}, and Zn^{2+}) are quite distincts, and so are the peak potentials for each one of them.

3.2 Controlled Potential Electrolysis at a Reticulated Nickel Foam Cathode

Observing the curve of Figure 6, for the potential sweep toward the reduction of Cd^{2+} ions, by using the reaction system of Figure 2, the current rises rapidly owing to the onset of the reduction of those ions transported to the cathode surface by convective diffusion. A well defined limiting current region is observed at a flow velocity of 0.2 m s^{-1}. The same trend was observed for the reduction of Cu^{2+} and Zn^{2+} even using different nickel foam grades and flow velocities.
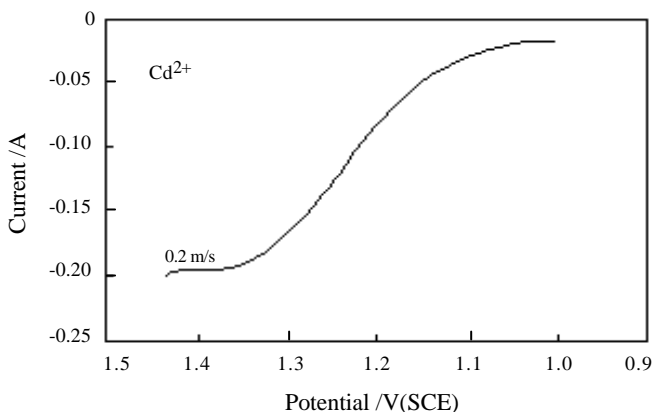
Figure 6 - Current *vs.* potential curve for the reduction of Cu^{2+} ions. [Cu] = 6.3 x 10^{-4} mol dm^{-3} , [K$_2$SO$_4$] = 0.5 mol dm^{-3}, scan rate = 0.01 V s^{-1} , flow velocity of 0.2 m s^{-1}. (7.5 x 10^{-5} m^3 s^{-1}) and a nickel foam with 35 p.p.i. and 2500 m^{-1}

The maximum yield for electrowinning Cu^{2+}, Cd^{2+} and Zn^{2+} was obtained at -1.0, 1.4 and 2.2 V(SCE) respectively, where the reactor system of the Figure 2 behaves as a continuously stirred tank reactor under mass transport control in a batch recycle mode. These figures suggest that selective separation is possible from dilute aqueous solutions like the ones from the desorption process of loaded brown seaweeds and from industrial electroplating operations as such.

4. CONCLUSIONS

Reticulated nickel foam, a recently developed form of three-dimensional electrode, can be successfully used as an electrode material to electrodeposit heavy metals like copper, cadmium and zinc from very dilute aqueous solutions.

High porosity and relatively higher specific surface area coupled with low cost of RNiF are the advantageous characteristics which make this material highly suitable for electrode construction for removing metals from dilute industrial effluents.

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