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New hybrid electrocoagulation membrane process for removing selenium from industrial wastewater

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Abstract

High concentrations of heavy metal cations such as Cd, Cu, Zn, Pb and Fe as well as heavy metal anions such as As and Se are contained in the wastewater generated by industrial Cu production. The conventional technology for treating this kind of wastewater, which consists of lime neutralisation/$FeCl_3$ coagulation and flocculation, does not satisfy the requirements for direct wastewater discharge which specify that Se concentration should be less than 30 µg/l. The residual selenium concentration, the large sludge quantities generated as well as the expense of reagents are just some of the shortcomings of this technology. To combat these problems, a new hybrid process combining electrocoagulation and microfiltration was drawn up and verified in experiments. Very good adsorption/co-precipitation properties for selenium removal were observed for iron hydroxide, generated by electrocoagulation although precipitation was difficult, due to the fines of sludge. Iron hydroxide could be completely removed from the water by applying an integrated filtration process involving submerged microfiltration flat sheet ceramic membranes (mean pore size of 0.3 µm). Furthermore, the cake, formed on the microfiltration membranes, could be used as a barrier adsorbent for reducing the residual Se. A new bench-scale electrocoagulation/membrane filtration cell was developed and optimised in experiments to test the new hybrid process. Firstly, very extensive optimisation experiments using model wastewater were performed followed by bench-scale experiments with real industrial wastewater from Cu production. Results showed that, at a continuous regime with a treatment time of 20 min and a current density of the anode of 4.8 mA/cm^2, Se reduction was 98.7%, As 99.9%, Cu and Pb more than 98.0%, Zn and Cd more than 99.9%.

Keywords: Industrial wastewater; Heavy metals; Selenium; Electrocoagulation; Microfiltration; Hybrid process

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1. Introduction

Industrial wastewater from Cu production has high concentrations not only of heavy metal cations (Cd, Cu, Zn, Pb, Fe), but also of heavy metal anions such as As (up to 500 mg/l) and Se as oxyanions at 2–3 mg/l (up to 6 mg/l in some partial streams). Most of the heavy metals, cations and anions, can be removed without problems, with the exception of Se, to achieve the discharge concentration required. The technologies for Se removal, experimented with and partially applied, are as follows [1]:

- precipitation as selenate, selenite, selenide or elemental selenium;
- adsorption on ferrihydrite, activated alumina, ferric oxyhydroxide (these processes are effective for the removal of Se (IV) but not for Se (VI));
- ion-exchange (this process is effective for the removal of Se (VI) rather than for Se (IV));
- reverse osmosis and nanofiltration (pre-treatment for reverse osmosis and nanofiltration is very complicated and the selectivity of the membrane, especially reverse osmosis, is very poor);
- emulsion liquid membranes (in this process, Se (VI) is extracted rapidly even in the presence of sulphate at all pH values >2 but Se (IV) extraction is influenced by the presence of sulphate);
- reduction processes (ferrous hydroxide, iron reductant etc.);
- biological processes: bacterial reduction with *Pseudomonas stutzeri* of selenium species Se (IV) and Se (VI) to elemental selenium has been shown to be a potential candidate for treating water containing Se. However, one problem is the high operating time and the size of the apparatus;
- conventional treatment: lime neutralisation-softening/ferric coagulation/flocculation/filtration. This is the best available technology (BAT) for the treatment of drinking and ground water as well as wastewater contaminated with metal but it is doubtful if selenium removal can comply with the regulations on direct discharge (Se concentration less than 30 µg/l). The drawbacks with this technology are the residual Se concentration of more than 30 µg/l, generation of large volumes of sludge and the high cost of reagents;
- hybrid processes such as coagulation/crossflow microfiltration [2], adsorption (ion exchange)/crossflow microfiltration, adsorption (ion exchange)/flotation/submerged microfiltration [3–8] have been mostly experimented with in the last decade for the removal of different impurities including heavy metals.

One of the promising methods for removing selenium and arsenic from water is the electrochemical method using dissolvable metal electrodes. Insoluble precipitates are obtained from the compounds of Se, As as well as other heavy metal ions with the ions of the dissolved metal electrode.

The most wide-spread electrochemical method for processing industrial wastewater appears to be the method of electrocoagulation, applied individually or in combination with other methods, e.g., electrocoagulation/flotation or crossflow microfiltration [2]. In electrocoagulation, chemical compounds, which adsorb the wastewater impurities, are obtained electrochemically. The water is treated in an electrolyser with graphite or stainless steel cathodes and Al, Fe, Zn, Ni etc anodes, depending on the impurities to be removed. As a result of electrolysis processes, the ion composition of the water around the electrodes is changed (more often due to the precipitation of heavy metals), as well as pH, oxidation/reduction potential (Eh), etc. The final composition of the water depends on its initial parameters, on the material and shape of electrodes as well as on electric current consumption. Normally, hydroxides, obtained electrochemically, have much higher sorption ability than those obtained chemically because of the finely dispersed structure and very well developed specific surface.

In this paper, the experimental results for the removal of Se by a new hybrid process [9] combining electrocoagulation and dead-end microfiltration with submerged ceramic, multi-channel flat-sheet membranes will be presented.

2. Materials and methods

The experimental set-up (primary lime neutralisation with sedimentation, electrocoagulation/microfiltration and final lime neutralisation with sedimentation), the electrodes for the electrocoagulation cell and the main operating parameters are shown in Figs. 1 and 2, respectively. Oxidation in the electrocoagulation cell was experimented with in two ways: with air directly into the cell and by H_2O_2 dosing before the cell. The submerged ceramic microfiltration membranes including the main membrane parameters in the hybrid electrocoagulation/microfiltration process are shown in Fig. 3.

3. Results

Extensive optimisation experiments with model wastewater were conducted. In Fig. 4, the Se and As removal kinetics of electrocoagulation using a model solution containing 5 mg/l Se and 100 mg/l As are shown.

Some experimental results for the proposed different treatment stages of the bench-scale experiments (primary lime neutralisation with sedimentation, electrocoagulation/microfiltration and final lime neutralisation with sedimentation) using real wastewater from Cu production are shown in Table 1 and Fig. 5. The continuous output of the electrocoagulation/membrane filtration

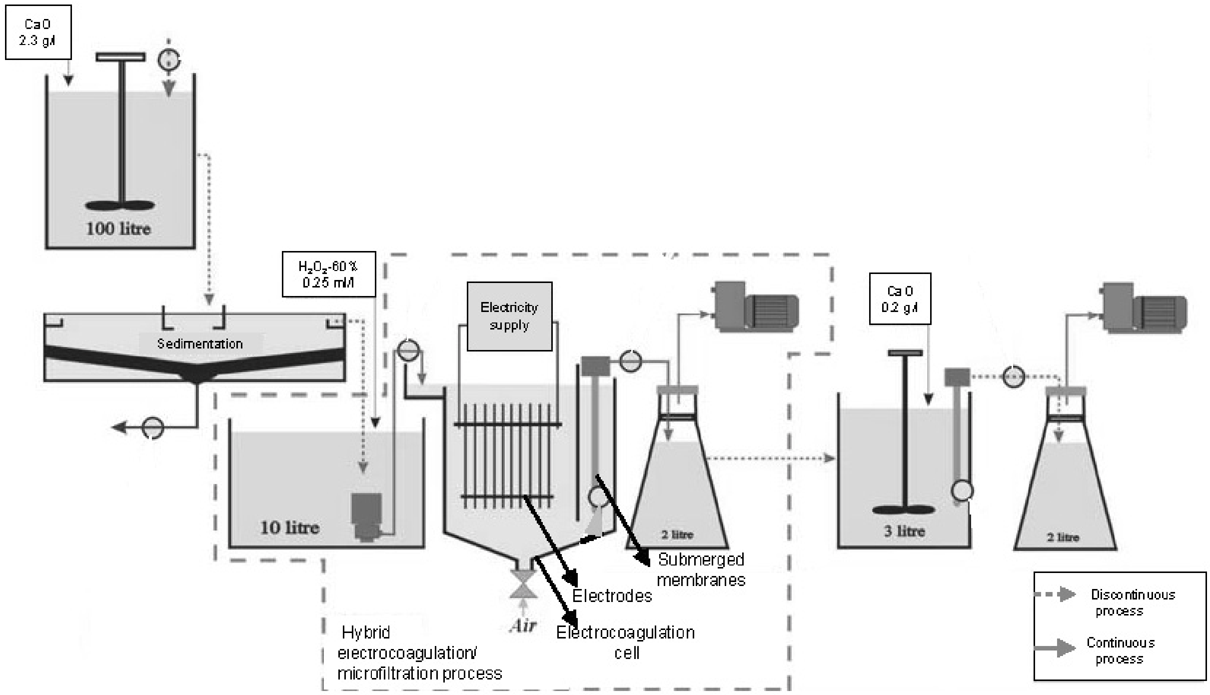
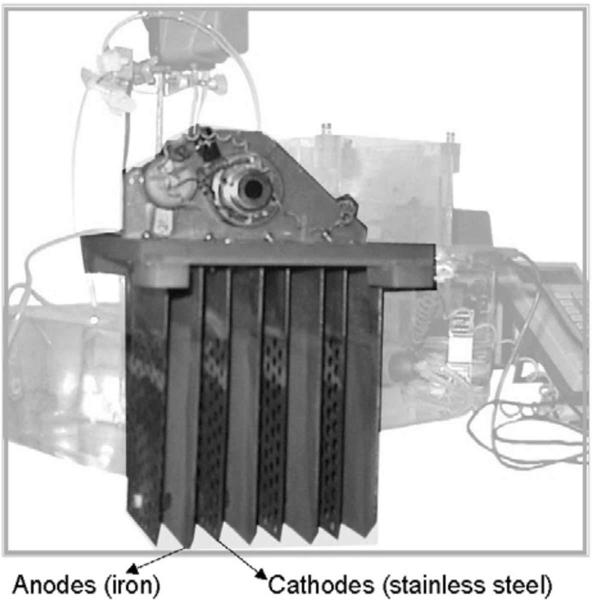
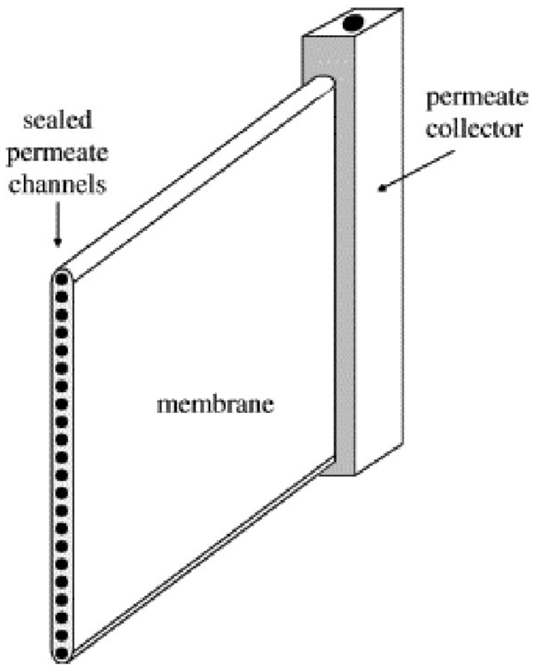


Fig. 1. Experimental set-up.



Cell volume	1.5 l
Volume of electrochemical module	1.0 l
Treatment time	5-20 min
Volume flow	3-10 l/h
Current density	5-10 mA/cm^2
El. Power	3-6 V
Aeration with air	For increasing process kinetics, oxidation and stirring of solution

Fig. 2. Electrodes for the electrocoagulation cell and main cell parameters.



Membrane	Microfiltration
Type	Multi-channel, flat-sheet
Material	Ceramic Al_2O_3
Geometry	100x100x6 mm
Mean pore size	0.3 µm
Surface	200 cm^2
Permeability (pure water)	3000 L m^{-2}h^{-1}bar^{-1}
Filtration mode	Dead-end vacuum filtration
Cleaning	Back-pulsed with air to remove filtration cake, if necessary back-flushing with water

Fig. 3. The submerged ceramic microfiltration membranes and the main membrane parameters.

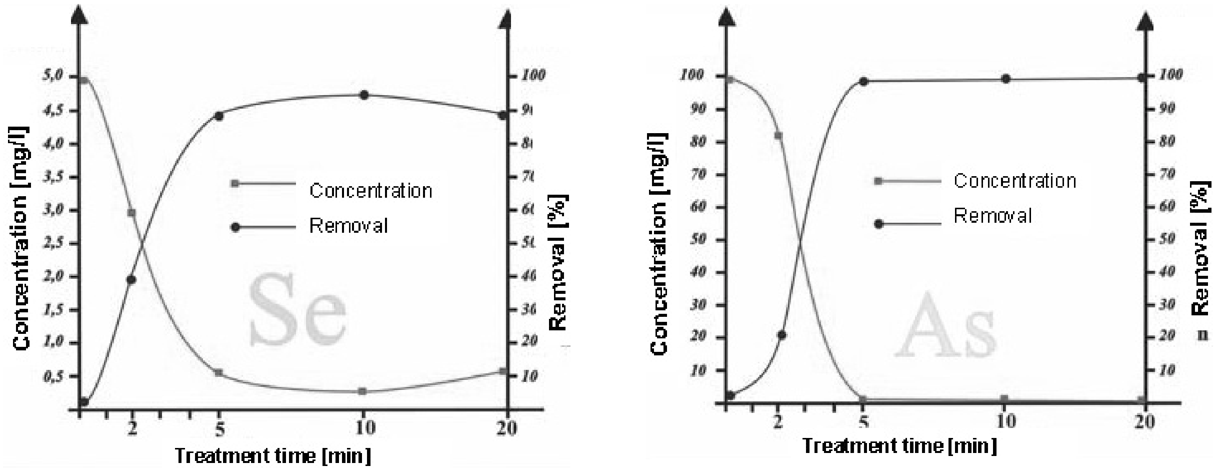


Fig. 4. Kinetic curves of Se and As removal with the model solution of 5 mg/l Se and 100 mg/l As (continuous regime, without oxidation, 6.8 mA/cm^2).

Table 1
Experimental data with real wastewater from Cu production (continuous regime, air oxidation, treatment time 20 min; 4.8 mA/cm^2)

Items	As (mg/l)	Fe (mg/l)	Cu (mg/l)	Se (mg/l)	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)	pH
Industrial wastewater	442.0	202.0	19.5	2.32	85.2	34.3	5.23	—
Primary lime neutralisation/ sedimentation								
Treated water	442.0	195.0	18.9	2.28	83.8	35.2	2.55	2.18
Sediment (%)	>0.001	0.05	0.004	0.0003	0.03	0.0007	0.02	—
Electrocoagulation/microfiltration								
Filtrate	1.85	471.0	0.36	0.03	12.5	8.09	0.1	4.43
Cake (%)	12.94	24.2	0.5	0.07	2.1	0.8	0.07	—
Final lime neutralisation/ sedimentation								
Treated water	<0.1	1.02	0.24	0.03	<0.1	<0.01	<0.1	9.51
Sediment (%)	0.1	24.7	—	<0.0001	0.7	0.4	—	—

stage was 3–6 l/h, treatment time 10–20 min and the current density of the anode 4.8–6.8 mA/cm^2. The submerged membrane showed permeate fluxes of between 150–500 l/m^{2}h at ΔP vacuum from 60 mbar to 680 mbar.

4. Discussion and conclusions

A new hybrid process of electrocoagulation and microfiltration was proposed and experimentally proven. The iron hydroxide, produced

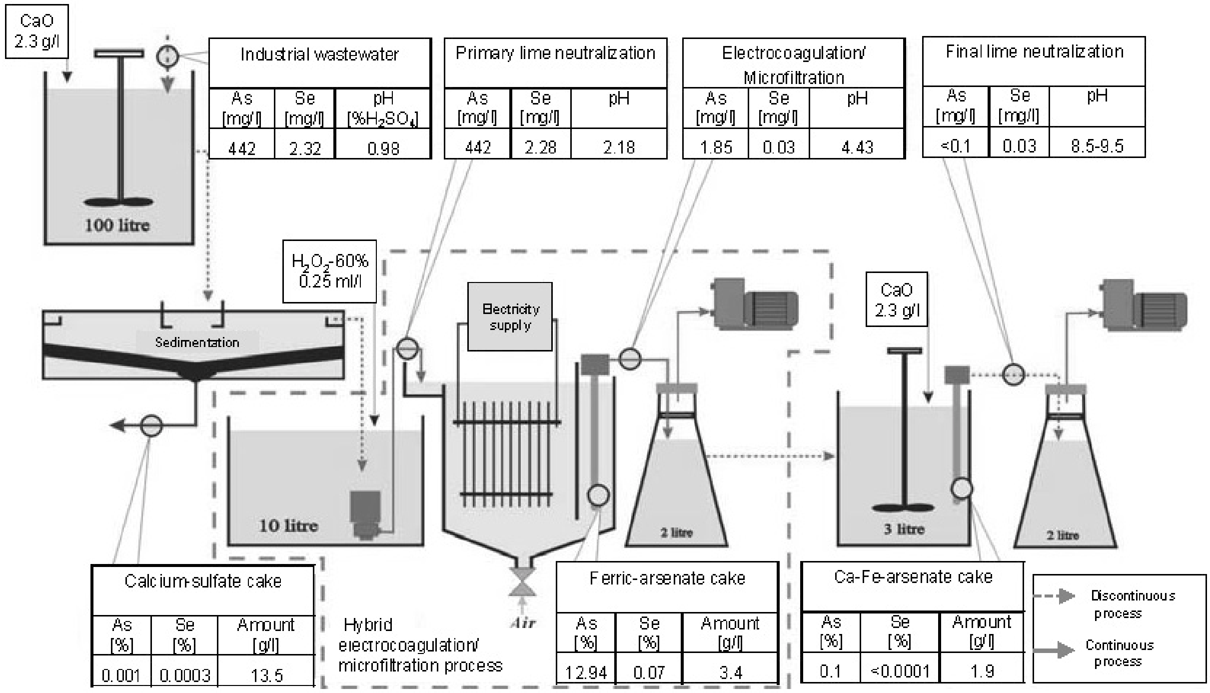


Fig. 5. Main experimental results of different treatment stages including hybrid electrocoagulation/microfiltration.

by electrocoagulation, has very good adsorption/co-precipitation properties for removing Se, but is very difficult to be precipitated, because of the fines of sludge. By means of integrated filtration of this "adsorbent" by submerged microfiltration flat sheet ceramic membranes (mean pore size of 0.3µm), the adsorbent Fe hydroxide is completely removed from the water and in addition the cake, formed on the microfiltration membranes, can be further used as a barrier adsorbent for reducing the residual Se.

In order to study this new hybrid process of electrocoagulation/MF membrane filtration, a new bench-scale electrocoagulation/membrane filtration cell was developed and optimised in experiments. Following very extensive optimisation experiments with model wastewater, bench-scale continuous on-site experiments with real industrial wastewater from Cu production were performed. It was shown that at a continuous regime with treatment time of 20 min and a current density of the anode of 4.8 mA/cm^2, a reduction of 98.7% was achieved for Se (for example Se_{Feed} = 2.32 mg/l, $Se_{Filtrate}$ = 0.03 mg/l) with a parallel reduction of more than 99.9% for As, more than 98.0% for Cu and Pb, and more than 99.9% for Zn and Cd, satisfying all the requirements for direct discharge of treated water.

The solid waste obtained from all the treatment stages (sediment from the primary neutralisation, filtration cake from electrocoagulation/membrane filtration and sediment from the final lime neutralisation) is roughly 40% less than the quantity of solid waste obtained in conventional lime neutralisation/ferric coagulation/filtration technology. The solid waste obtained is practically insoluble and stable in a wide pH range of 2–10, thus allowing its disposal without any special equipment at high cost. The proposed technology with the use of electrocoagulation/

membrane filtration needs roughly 15% less chemicals compared with conventional processes. Submerged microfiltration using ceramic membranes shows very stable filtration operation with easy removal of the filtration cake by back-pulsed air.

The proposed new hybrid process of electrocoagulation/membrane filtration shows very promising results for solving the problem of Se removal as well as other metals (especially As, Cu, Pb) in the treatment of industrial wastewater.

5. Acknowledgements

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