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Removing heavy metals by electrocoagulation using stainless steel mesh electrodes: a study of wastewater from soil treated with metallurgical residues

Remoção de metais pesados por eletrocoagulação utilizando eletrodos de malha de aço inoxidável: um estudo de águas residuais provenientes de solo tratado com resíduos metalúrgicos

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Abstract

The present work aims to study the possibility of zinc, cadmium and manganese removal from synthetic solutions simulating wastewater from washing soil by electrocoagulation process using stainless steel mesh electrodes.The influences of current density (from 10 to 40 mA cm-2), time (20 and 40 minutes) and pH (4 to 10) on removal efficiency were explored in a batch cell to determine the best experimental conditions. Under the operating conditions tested, the best result was observed at pH = 10, corresponding to about 90% of heavy metals removal from solutions initially containing 15 mg dm-3 of each metal, with a power consumption of 9 kW h m-3.There are few published studies using stainless steel electrodes for the treatment of mixed heavy metals and this study newly indicated that the proposed method is adequate to remove the common heavy metals found in wastewater from heavy metals polluted soil.

Keywords

new electrode, wastewater treatment, flotation.

Resumo

O presente trabalho tem como objetivo estudar a possibilidade de remoção de zinco, cadmio e manganês de soluções sintéticas que simulam efluentes provenientes da lixiviação de solos contaminados, por processo de eletrocoagulação utilizando eletrodos de malha de aço inoxidável. As influências da densidade de corrente (de 10 a 40 mA cm^{-2}), tempo (20 e 40 minutos) e pH (4-10) na eficiência de remoção foram exploradas numa célula em batelada para determinar as melhores condições experimentais. Sob as condições de funcionamento testadas, o melhor resultado foi observado a um pH = 10, correspondendo a cerca de 90% de remoção de metais pesados a partir de soluções contendo inicialmente 15 mg dm^{-3} de cada metal, com um consumo de energia de 9 kWh m^{-3}. Existem poucos estudos publicados utilizando eletrodos de aço inoxidável para remoção simultânea de metais pesados e este estudo indicou que o método proposto é eficiente para eliminar os metais pesados comuns encontrados em águas residuárias.

Palavras-chave

novo eletrodo, tratamento de águas residuais, flotação.

Como você deve citar?

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1 INTRODUCTION

The industrial advance has generated a large quantity and variety of waste that causes serious environmental problems. On the one hand, the proper disposal of residue constitutes in a need for public health, environmental preservation and social responsibility. On the other, the return of organic matter and nutrients to the soil can contribute to produce food and biofuels (ROSSOL et al., 2012).

The use of metallurgical residues in agriculture, like basic slag, mill scale, filter press mud and phosphate mud, has been widely discussed, based on studies which indicate it can improve the physical-chemical properties of the soil, increase the biological activity and contribute to the recycling of nutrients. However, it is necessary to consider the presence of potentially toxic heavy metals in these residues, particularly cadmium (Cd), zinc (Zn), manganese (Mn), copper (Cu) and lead (Pb), which are bioaccumulative and carcinogenic (SOBRAL et al., 2011).

Although Cu and Zn are micronutrients to the plants, according to the amount, it can become toxic and cause environmental pollution. Contamination of groundwater from heavy metals depends on the concentration and solubility of these metals, the amount of waste added to the soil, local precipitation and mobility of these species. Already, the greater or lesser mobility is influenced by the soil characteristics and the metal content. Studies on the mobility of heavy metals in soil have shown that Pb, Cr and Cu have low mobility and accumulation on the surface of contaminated soil. On the other hand, Zn, Cd and Mn are more mobile in the soil profile, representing an increased risk of aquifer pollution (NASCIMENTO et al., 2010).

The water quality protection and also the removal of specific compounds arising from different aqueous systems require the study of economic, ecological and efficient methods. Such studies are important mainly for the aqueous systems containing metallic ions in low concentrations. Due to simplicity and its low cost of operation, the electrocoagulation (EC) can be considered as a potential purification technique that involves applying an electric current in sacrificial electrodes inside a reactor where the current generates a coagulating agent and gas bubbles. The basis of electrocoagulation is the *in situ* formation of coagulant species that can remove various pollutants from the wastewater under treatment, which are retained in the supernatant foam (LU et al., 2015).

According to Mollah et al. (2004), EC process involves three successive stages:

1. Formation of coagulants by metal (M) anode dissolution, in addition, water electrolysis occurs at the cathode and anode:

$$M_{(s)} \longrightarrow M^{n+}_{(aq)} + n\ e \qquad \text{(anode)} \qquad (1)$$

$$H_2O_{(l)} \longrightarrow 2\ H^{+}_{(aq)} + ½\ O_{2\ (g)} + 2e \qquad \text{(anode)} \qquad (2)$$

$$2\ H_2O_{(l)} + 2\ e \longrightarrow H_{2\ (g)} + 2\ OH^{-}_{(aq)} \qquad \text{(cathode)} \qquad (3)$$

2. Destabilization of the contaminants. A direct electrochemical reduction of metal cations (M^{n+}) may occur at the cathode surface. Moreover, the hydroxide ions formed at the cathode increases the pH of the wastewater producing metal hydroxides.

$$M^{n+} + n\ e \ n\ M^0 \qquad (4)$$

$$M^{n+} + n\ OH^-\ M(OH)_{n\ (s)} \qquad (5)$$

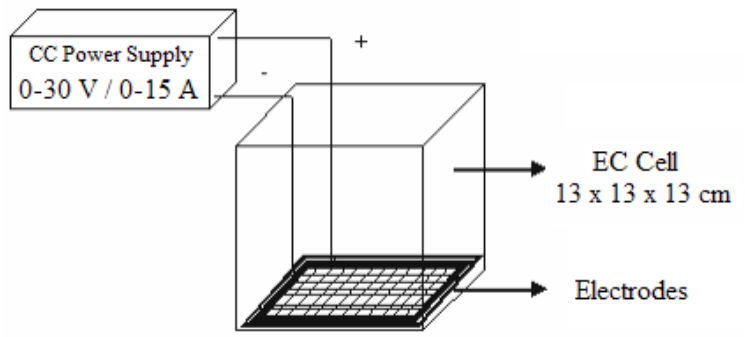
3. Aggregation of the destabilized phases to form flocs.

The aim of this research is to remove Zn, Cd and Mn ions from aqueous solution that simulates a resulting effluent from the percolation of a soil treated with metallurgical waste by EC, using stainless steel mesh electrodes.

2 MATERIAL AND METHODS

The EC experiments have been performed in a batch cell with 2 electrodes, located on the flotation cell bottom. The distance between both electrodes was *e* = 1.0 cm and the experimental setup is shown in Figure 1.

Figure 1 - Bench-scale EC reactor.



Fonte: dos autores.

2.1 Construction of the electrodes

Stainless steel wires with 0.04 cm of diameter were used as electrodes. Therefore, it was necessary to assemble a frame from one acrylic plate available to provide support for the wires. In this square frame, 1 cm wide, 7 holes were made on each side so that the wires were tressed. A digital CC power supply (0-30 V, 0-15 A) was used to give regulated electricity current to the EC cell.

The number of holes present in the frame and the number of times that the wires were passed into each hole determined the useful area of each electrode. Thus, it was possible to estimate the highest and lowest current density in this system. Table 1 shows the useful areas of stainless steel electrodes as a function of the number of holes in the frame and the number of times the wire is passed into each hole.

Table 1 - Useful areas of the electrodes

	14 holes	28 holes
Single pass in each hole	10.6 cm^2	21.2 cm^2
Double pass in each hole	21.1 cm^2	42.4 cm^2
Triple pass in each hole	31.8 cm^2	63.6 cm^2

Fonte: dos autores.

Current density is the most important parameter for controlling the reaction rate in EC process because it determines the reaction rate of electrodes. It is known that current density (was defined by:

$$\rho_A = \frac{i}{S} \quad (6)$$

where *i* and S represent the current (A) and the useful area of the electrode (cm^2, dm^2 or m^2), respectively.

Bibliography listed in Table 2 supports the number of holes and the number of times that the wires were passed into each hole. Choosing an useful area of 42 cm^2 approximately, the lowest and higher (highest) current density possible for this EC system are 0 and 0.36 A cm^{-2}, respectively. But the experimental conditions studied admit the current density until 40 mA cm^{-2}, which is consistent value, as observed in Table 2.

Table 2 - Bibliography used as an object of study of handmade electrodes.

Reference	Pollutant	Current density	Electrodes	Efficiency (maximum)
LU et al. (2015)	Ni^{2+}	2.5 – 27.5 A m^{-2}	Aluminum	98%
TAK et al. (2015)	Color and chemical oxygen demand (COD)	10 – 30 mA cm^{-2}	Aluminum	93%
MOHORA et al. (2014)	Arsenic from groundwater	8.86 mA cm^{-2}	Aluminum	89%
RICORDEL and DJELAL (2014)	Color and COD from landfill leachate	23 – 95 A m^{-2}	Aluminum	80%
VU et al. (2014)	Powdered activated carbon from urban wastewater	100 – 1000 A m^{-2}	Aluminum and stainless steel	95%
ORKUN and Kuleyin (2012)	COD from landfill leachate	30 mA cm^{-2}	Iron	66%
CHAFI et al. (2011)	Color of a synthetic textile wastewater	7.5 – 65 mA cm^{-2}	Iron and Aluminum	98%

Fonte: dos autores.

2.2 Electrocoagulation process

Stock solutions containing 15 mg dm^{-3} of Zn, Cd and Mn were prepared with sulfate salts of each metal. With the aim of increasing the removal efficiency, a supporting electrolyte (sodium sulfate) was added to grow the ionic strength to reduce the resistance between the electrodes. The analytical grade chemicals used were listed as follows: zinc sulfate (VETEC, Brazil), cadmium sulfate (VETEC, Brazil), manganese sulfate (VETEC, Brazil), sodium sulfate (VETEC, Brazil), sodium dodecil sulfate (B'HERZOG, Brazil), sulfuric acid (VETEC, Brazil), sodium hydroxide (VETEC, Brazil), ethyl alcohol (B'HERZOG, Brazil) and distilled water.

In each batch, one liter of synthetic wastewater was added to the flotation cell. The collector, sodium dodecyl sulfate (SDS) was added in the correct ratio as well as the pH regulators and bubbly agent (ethyl alcohol, 0.1% vol.). The CC font was turned on and the procedure was initiated. All the runs were carried out at 28ºC and to follow the progress of the EC process, samples of 15 mL were periodically taken from the electrocoagulation cell. The residual concentrations of metal ions were determined by an atomic absorption spectrophotometer (VARIAN 600 SB). The pH was monitored with a pH-meter (ION, pHB 500).

Before each run, the electrode surface was first mechanically polished with steel wool, rinsed with distilled water and dried.

The removal efficiencies (η) of zinc were evaluated by the following universal equation (MAHMOUD et al., 2013):

$$\eta_{(\%)} = \left(\frac{C_0 - C}{C_0}\right) 100 \quad (7)$$

Co and *C* are respectively the concentrations ions before and after the treatment.

In order to measure the rise bubbles velocity, a graduated ruler was fixed on EC cell and images were recorded (Nikon D3200). Finally, the amount of electrical energy used was calculated by Equation 8 (MANSOORIAN et al., 2014):

$$E = \frac{U\ i\ t}{V} \quad (8)$$

E is the electrical energy used (in kW h m^{-3}), U is the voltage used (in V), I is the current (in A), t is the coagulation time in hours, V is the volume in liters.

3 RESULTS AND DISCUSSION

The electrocoagulation is affected by several operating parameters, such as current density, contact time and initial pH. In this study, all these parameters were explored in order to evaluate a treatment technology for Zn, Cd and Mn removal from a synthetic wastewater. In the first stage, experimental studies were carried out at different current densities: 10, 20, 30 and 40 mA cm^{-2}, with different contact time (20 and 40 minutes) with 15 mg dm^{-3} of initial metal concentrations and 0.003 M of supporting electrolyte concentration at pH=7.0 of the solutions.

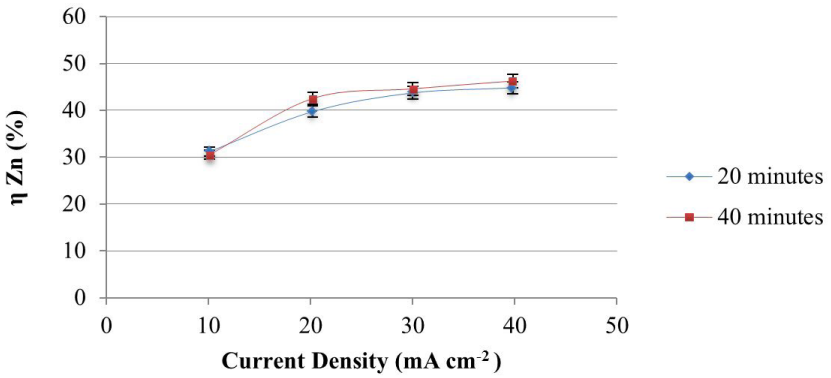
Previous works on ion flotation have indicated that the use of specific stoichiometric ratios of collectors plays an important role in the removal performance. When 1:1 collector:colligant ratio is used a very thin and unstable foam layer is formed at the top of the cell, so an excess of collector is always indicated to ensure the formation of sublates. In this work, SDS is used in the stoichiometric ratio equal to 1:3 in all tests.

For the second stage of experiments, studies were carried out at different initial pHs of 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 at the current density of 30 mA cm^{-2}, with 15 mg dm^{-3} of initial metal concentrations and 0.003 M of supporting electrolyte concentrate.

3.1 Effect of current density and contact time

This EC process used a current power source between steel mesh electrodes immersed in polluted water. It is known that the current density determines Fe^{2+} ions released by the anode dissolution into wastewater, adjusts bubble production, its distribution, and hence affects the growth of flocs $Fe(OH)_{2(s)}$ or $Fe(OH)_{3(s)}$. Figure 2 shows the effect of current densities on the zinc removal rate of a solution containing Zn, Cd and Mn. The results indicated that the removal rates increased, as expected, with increasing current density.

Figure 2 - Effect of current densities and contact time on the residual concentrations of zinc.



Fonte: dos autores.

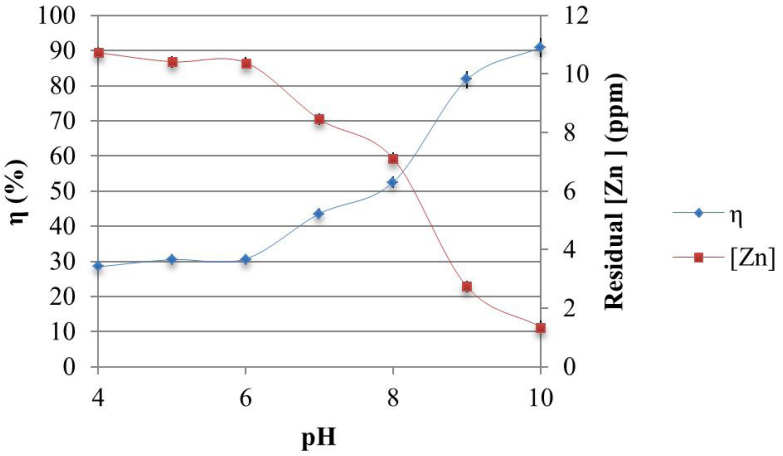
Current density studies were accomplished at pH= 7.0 and were followed by the study of the optimal time. It is observed that the removal rate was slightly higher for 40 minutes at higher current density evaluated. However, energy consumption is directly related to the current density and time of EC process. So, despite the best results, it is not economically favorable to choose 40 minutes as great contact time and 40 mA cm^{-2} as the best current density.

The kinetics of flotation has been studied by other authors (MOTA et al., 2015; HANAY et al., 2011; JUNG, 2002; FUKUY, 1994) and conclusions are that: regardless of the process employed in the flotation, air dispersed, dissolved air or EF, or the material removal, suspended solids, oils or heavy metals, after 20 or 30 minutes of operation, the efficiency reaches its final levels. Therefore, in this work, the optimal flotation time and current density were set at 20 minutes and 30 mA cm^{-2}.

3.2 Effect of initial pH

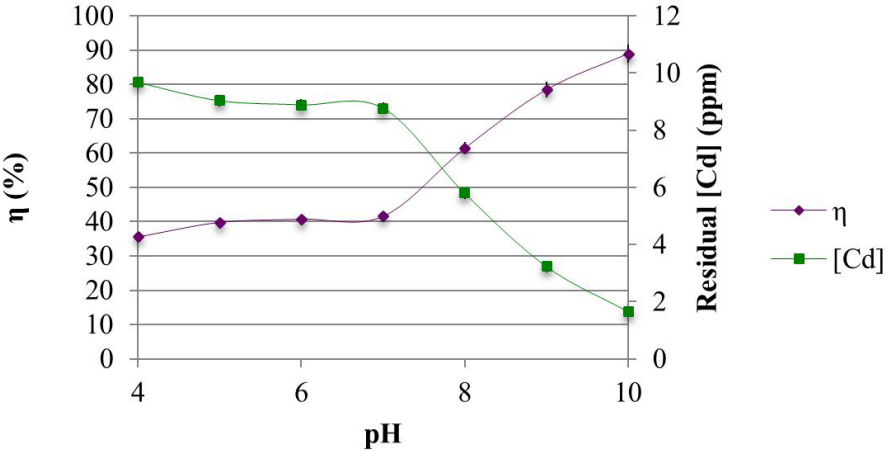
Heavy metal removal by EC has a mechanism that is highly sensitive to the pH solution as can be seen in Figure 3. Figure 3 (a), Figure 3 (b) and Figure 3 (c) show removal efficiencies of simultaneous removal and residual concentrations of Zn, Cd, Mn, respectively, as a function of initial pH solutions.

Figure 3. Effect of initial pH on the residual concentrations and removal efficiencies of heavy metals.
Figure (a)



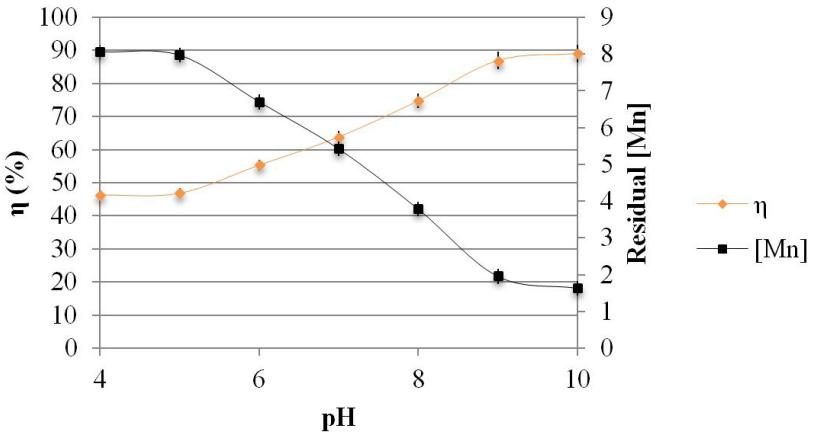
Fonte: dos autores.

Figura 3 (b)



Fonte: dos autores.

Figura 3 (c)



Fonte: dos autores.

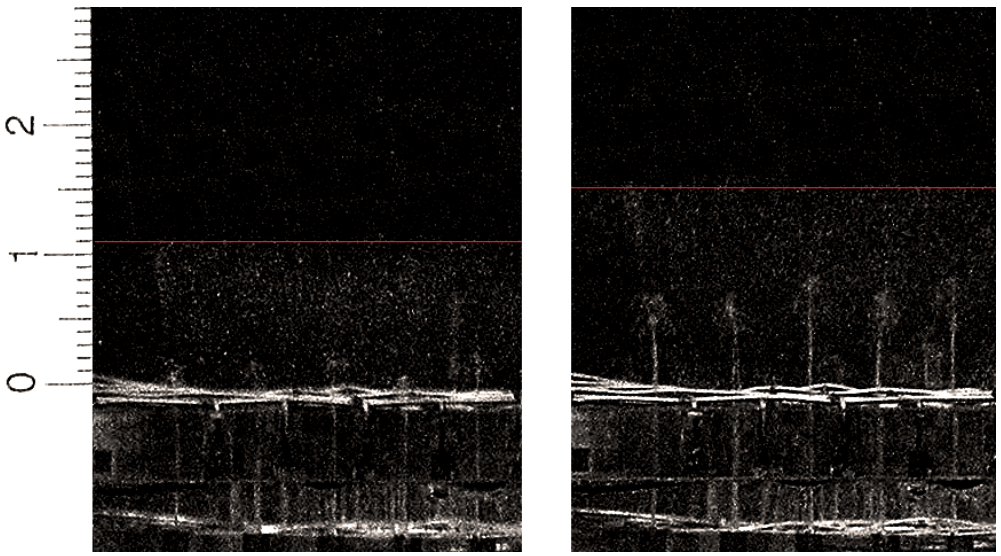
The results showed in Figure 3 indicated that the best removals for three metals were achieved with increasing the pH. Similar results were found by Mota et al. (2015) and Hanay at al. (2011) for Zn and Cd removal from solutions with different heavy metals combinations. A treatment for 20 minutes, at a current density of 30 mA cm^{-2}, removed around 90 % of Zn, Cd, Mn at pH= 10.0. This result is related to availability of basic species, which indicates that the best results were obtained in a range of precipitate flotation.

3.3 Study of bubbles velocity

The flow of bubbles influences the kinetics of flotation process affecting the retention time of the metal in the flotation cell. The photos taken were converted to gray scale, through the software *NIH ImageJ,* to facilitate visualization of the bubbles ascension. The result can be seen in Figure 4, generated at a current density of 30 mA cm^{-2}.

Figure 4 - (a) Image 01: bubbles generation at time t=0s. (b) Image 02: bubbles generation at time t=1s.

(a) (b)



Fonte: dos autores.

Boundary lines (in red) were marked to estimate the rise velocity of bubbles, which was 0,4 $cm.s^{-1}$. From the estimated average speed, it was possible to estimate the residence time of the bubbles in the cell: approximately 25 seconds, at 28°C. The methodology was considered consistent according to literature (KOTTI et al., 2013).

Other studies have investigated the effect of bubbles rise velocity on the removal rate and it was concluded that as the flow of bubbles increases, the recovery of the species becomes faster. However, at high rates, removal of the ions becomes incomplete due to redispersion of the sublate in the turbulent solution. On the other hand, low levels of bubbles require longer retention time, the collection form depends on the ion collector and against colligant the bubble surface, the residence time of the bubbles should be sufficiently high to allow the process to be completed (SARKAR et al., 2010; LIUYI et al., 2014).

3.4 Energy consumption

Under the experimental conditions studied, it has been found that the voltage increased linearly with the current applied on electrodes. In optimal operating conditions, the maximum energy consumption was 9 kW h m^{-3}, which represents a relative low cost of the treatment when compared with other researches who used other types of electrodes (DANESHVAR et al., 2007; MARTÍNEZ-VILLAFAÑE et al., 2009; FAJARDO, et al., 2015).

4 CONCLUSION

A new stainless steel electrode was evaluated for the removal of heavy metal from synthetic solutions simulating wastewater from washing soil. Through the proposed system it was possible to remove around 90% of Zn, Cd and Mn by EC, with low energy consumption of 9 kW h m^{-3}, from solution containing 15 mg L^{-1} of each metal, using sodium dodecyl sulfate (SDS) as collector in the stoichiometric ratio 1:3, current density around 30 mA cm^{-2}, 0.1% ethanol (as a frother) and 0.003 M of supporting electrolyte concentrate. In this study it was found that the best condition was achieved at pH = 10.

Overall, the study affirmed that electrocoagulation is a reliable and environmentally compatible technique for the purification of water, industrial effluent, groundwater and mineral processing with high efficiency, specially for dilute systems.

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REFERENCES

CHAFI, M.; GOURICH, B.; ESSADKI, A. H.; VIAL, C.; FABREGAT, A. Comparison of electrocoagulation using iron and aluminium electrodes with chemical coagulation for the removal of a highly soluble acid dye. **Desalination,** v. 281, p. 285–292, 2011.

DANESHVAR, N.; KHATAEE, A. R.; GHADIM, A. R. RASOULIFARD, M. H. Decolorization of C. I. Acid Yellow 23 solution by electrocoagulation process: Investigation of operational parameters and evaluation of specific electrical energy consumption (SEEC). **Journal of Hazardous Materials,** v. 148, n. 3, p. 566–572, 2007.

FAJARDO, A. S.; RODRIGUES, R. F.; MARTINS, R. C.; CASTRO, L. M.; QUINTA-FERREIRA, R. M. Phenolic wastewaters treatment by electrocoagulation process using Zn anode. **Chemical Engineering Journal,** v. 275, p. 331–341, 2015.

FUKUI, Y.; YUU, S. Development of Apparatus for Electroflotation. **Chemical Engineering Science,** v. 39, n. 6, p. 939-945, 1984.

HANAY, O.; HASAR, H. Effect of anions on removing Cu^{2+}, Mn^{2+} and Zn^{2+} in electrocoagulation process using aluminum electrodes. **Journal of Hazardous Materials,** v. 189, p. 572–576, 2011.

JUNG, Y. K.; HAN, M. Y. Simultaneous Removal of Cadmium and Turbidity in Contaminated Soil-Washing Water by Electroflotation. **Water Science Technology,** v. 46, n. 11-12, p. 225-230, 2002.

KOTTI, M.; KSENTINI, I.; BEN MANSOUR, L. Bubble hydrodynamic influence on oxygen transfer rate at presence of cationic and anionic surfactants in electroflotation process. **Journal of Hydrodynamics**, v. 25, n. 5, p. 747-754, 2013.

LIUYI, R. YIMIN, Z. WENQING, Q; SHENXU, B.; WANG, P.; CONGREN, Y. Investigation of condition-induced bubble size and distribution in electroflotation using a high-speed camera. **International Journal of Mining Science and Technology,** v. 24, p. 7-12, 2010.

LU, J.; LI, Y.; YIN, M.; MA, X.; LIN, S. Removing heavy metal ions with continuous aluminum electrocoagulation: A study on back mixing and utilization rate of electro-generated Al ions. **Chemical Engineering Journal**, v. 267, n. 1, p. 86-92, 2015.

MAHMOUD, M. S.; FARAH, J. Y.; FARRAG, T. E. Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes. **Egyptian Journal of Petroleum,** v. 22, n. 1, p. 211–216, 2013.

MANSSORIAN, H. J.; MAHVI, A. H.; JAFARI, A. J. Removal of lead and zinc from battery industry wastewater using electrocoagulation process: Influence of direct and alternating current by using iron and stainless steel rod electrodes. **Separation and Purification Technology,** v. 135, p. 165–175, 2014.

MARTÍNEZ-VILLAFAÑE, J. F.; MONTERO-OCAMPO, C.; GARCÍA-LARA, A. M. Energy and electrode consumption analysis of electrocoagulation for the removal of arsenic from underground water. **Journal of Hazardous Materials,** v. 172, n. 2-3, p. 1617-1622, 2009.

MOHORA, E.; RONCEVIC, S.; AGBABA, J.; TUBIC, A.; MITIC, M.; KLAŠNJA, M.; DALMACIJA, B. Removal of arsenic from groundwater rich in natural organic matter (NOM) by continuous electrocoagulation/ flocculation (ECF). **Separation and Purification Technology,** v. 136, p. 150–156, 2014.

MOLLAH, M. Y. A.; MORKOVSKY, P.; GOMES, J. A. G.; KESMEZ, M.; PARGA, J.; COCKE, D. L. Fundamentals, present and future perspectives of electrocoagulation. **Journal of Hazardous Materials**, v. 114, p. 199–210, 2004.

MOTA, I. O.; CASTRO, J. A.; CASQUEIRA, R. G.; OLIVEIRA JUNIOR, A. G. Study of electroflotation method for treatment of wastewater from washing soil contaminated by heavy metals. **Journal of Materials Research and Technology,** v. 4, n. 2, p. 109-113, 2015.

NASCIMENTO, R. S. M. P; CARVALHO, G. S.; PASSOS, L. P.; MARQUES, J. J. Lixiviação de chumbo e zinco em solo tratado com resíduos de siderurgia. **Pesquisa Agropecuária Tropical**, v. 40, n. 4, p. 497-504, 2010.

ORKUN, M.O.; KULEYIN, A. Treatment performance evaluation of chemical oxygen demand from landfill leachate by electro-coagulation and electrofenton technique. **Environmental Progress & Sustainable Energy**, v. 31, n. 1, p. 59-67, 2012.

RASBAND, W. S. IMAGE J. U. S. National Institutes of Health, Bethesda, Maryland, In: <http://rsb.info.nih.gov/ij/>, 1997-2008.

RICORDEL, C.; DJELAL, H. Treatment of landfill leachate with high proportion of refractory materials by electrocoagulation: System performances and sludge settling characteristics. **Journal of Environmental Chemical Engineering,** v. 2, p. 1551–1557, 2014.

ROSSOL, C. D.; SCALON FILHO, H.; BERTÉ, L. N.; JANDREY, P. E.; SCHWANTES, D.; GONÇALVES JR, A. C. Caracterização, classificação e destinação de resíduos da agricultura. **Scientia Agraria Paranaensis**, v.11, n. 4, p. 33-43, 2012.

SARKAR, M. S. K. A; DONNE, S. W.; EVANS, S. W. Hydrogen bubble flotation of Silica. **Advanced Powder Technology,** v. 21, p. 412 – 418, 2010.

SOBRAL, M. F.; NASCIMENTO, C. W. A; CUNHA, K. P. V; FERREIRA, H. A.; SILVA, A. J.; SILVA, F. B. V. Basic slag and its effects on the concentration of nutrients and heavy metals in sugarcane. **Revista Brasileira de Engenharia Agrícola e Ambiental**, v. 15, n. 8, 2011.

TAK, B.; TAK, B.; KIM, Y.; PARK, Y.; YOON, Y.; MIN, G. Optimization of color and COD removal from livestock wastewater by electrocoagulation process: Application of Box–Behnken design (BBD). **Journal of Industrial and Engineering Chemistry**, v. 28, p. 307–315, 2015.

VU, T. P.; VOGEL, A.; KERN, F.; PLATZ, S.; MENZEL, U.; GADOW, R. Characteristics of an electrocoagulation–electroflotation process in separating powdered activated carbon from urban wastewater effluent. **Separation and Purification Technology**, v. 134, n. 25, p. 196–203, 2014.