

USE OF MACROPHITES FOR REMOVAL OF Co e Zn IN LIQUID EFFLUENTS

Juliana de Almeida S. Oliveira and Paulo Sergio Cardoso da Silva

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
ju_aso@usp.br
pscsilva@ipen.br

ABSTRACT

This study proposes the application of *Eichhornia crassipes* roots biomass to remove cobalt and zinc ions from solution, aiming its application to effluent treatment. The efficiency of adsorption and the percent of removal were checked as a function of pH and contact time. The plants, for biomass production, were collected at the Billings reservoir in São Bernardo do Campo, located in the Southeast of São Paulo Metropolitan Region. The biomass obtained was subjected to the chemical activation process by the treatment with HCl 0.1 molL⁻¹ in order to increase its surface area. The concentrations of cobalt and zinc, present in the adsorbent, before and after the adsorption experiments were determined by the instrumental neutron activation analysis (INAA) technique. Results showed that the pH of the solution must be adjusted after the addition of the biomass. The contact time for maximum removal of both ions is between 20 and 30 min.

1. INTRODUCTION

The growing in the industrial activity has also led to increasing ecosystem contamination problems, mainly in aquatic environment, due to the discharge of untreated sewage, runoff water and wastewater [1]. Among the several substances released to the environment due to human activities, inorganic pollutants such as metal ions are in group of major concern [2] and many methods has been employed to remove metal ions from solution including chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc [3].

Besides these traditional methods for metal ion removal, several researchers have reported the potential use of biomass obtained from cow dung [4], agricultural waste [5], common reed [6], and peanut hull [7] as good adsorbents. Among the diversity of kind of biomass the use of macrophytes also emerges as a simple and low cost alternative [8]. Macrophytes are aquatic plant of rapid growing that grows emerged, submerged, or floating in water. The uncontrolled growing of these plants in the aquatic system is also one of the responsible for the eutrophication process that can result in oxygen depletion of the water body. Therefore the use of biomass of macrophytes as adsorbents can also help to solve this other environmental problem.

In adsorption studies it is common to use a chemical or physical activation of the adsorbent. The purpose of this activation is to increase the surface area of the solid by increasing its porosity [9]. Activation may produce structural defects in the adsorbent which, in turn, may favor the adsorption process.

The objective of this study was to verify the influence of pH and the contact time in the adsorption capacity of the acid activated roots of *Eichhornia crassipes*, known as aguapé, in the removal of cobalt (Co) and zinc (Zn) from aqueous solution. *Eichhornia crassipes* is a fast growing macrophyte vascular plant commonly found in all the Brazilian territory.

2. MATERIAL AND METHODS

The plants samples for biomass production were collected around the Billings reservoir in the city of São Bernardo do Campo, in the metropolitan region of São Paulo, where they are found in large quantities.

To obtain the biomass, in the laboratory, the roots of the collected plants were separated, washed with plenty of water to remove sediment and insects. They were oven dried at 60 ± 10 °C until constant weight, crushed until powdered to a particle size of 150 μm , treated with 0.1 mol L^{-1} HCl for 24 hours and dried in the oven at 40 °C to constant weight.

The solutions containing Co and Zn ions used in the experiments were prepared by diluting standard solutions (SPEX Certiprep) with concentrations of 1000 mg L^{-1} .

To evaluate the pH effect on the adsorption process, 0.5 g of the dried acid activated root was added to 20 mL of the solutions contained Co or Zn ions. The initial pH of the solutions was 2, 4, 6, 8, and 10. The mixtures were agitated by 20 min at 60 rpm and after that, the solid phase was separated by centrifugation at 3 500 rpm. The solid was dried in a ventilated oven separated for analysis.

To evaluate the effect of the contact time, 0.5 g of the adsorbent were added to 20 mL of the Co and Zn solution and the pH was adjusted to 6. The mixtures were agitated by 10, 20, 30, 60 and 120 min at 60 rpm and it was repeated the process described above. All the experiments were made in duplicate.

The concentrations of Co and Zn in the adsorbent before and after adsorption experiments were determined by neutron activation analysis. Approximately 100 mg of the dried solid adsorbent was packed in polyethylene bags together with the reference materials Marine Sediment (MESS-3) from the National Research Council of Canada and Marine Sediment, JMS-1 from the Japan Geochemical Reference Materials whose values for Co and Zn are certificated. The irradiation was done under a neutron flux of $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ at the IEA-R1 research nuclear reactor at IPEN, for a period of 8 hours. After the irradiation, the samples and reference materials were measured by gamma spectrometry after a cooling time of approximately 15 days.

For the gamma spectrometry it was used an EG&G Ortec HP-Ge detector, with a nominal efficiency of 20% and a resolution (FWHM) of 0.80 keV for the photopeak of 122 keV for ^{57}Co and 1.80 keV for the photopeak of 1332 keV of ^{60}Co , and associated electronics.

3. RESULTS AND DISCUSSION

Different sample collections were made for the pH and contact time effects determination and for each collection the Co and Zn concentration in the raw and in the acid activated roots of *Eichhornia crassipes* were determined. These results and the initial concentration in the solutions used are shown in Table 1. Cobalt concentrations presented small variations between the two sampling campaigns and between untreated and acid activated root biomass. Zinc, on the other hand, showed different amount in both cases. Zinc concentration was significantly higher in the second sampling campaign, and untreated root biomass presented significantly higher amount compared to acid activated ones.

Table 1: Concentrations of Co and Zn in the untreated and acid activated biomass obtained from *Eichhornia crassipes* and in the initial solutions used in the experiments.

	Co		Zn	
pH experiments				
untreated root ($\mu\text{g g}^{-1}$)	1.04	0.06	45	2
untreated root ($\mu\text{g g}^{-1}$)	0.9	0.1	18	1
initial solution (mg L^{-1})	0.120	0.004	1.2	0.1
Contact time experiments				
untreated root ($\mu\text{g g}^{-1}$)	1.34	0.04	163	4
untreated root ($\mu\text{g g}^{-1}$)	0.81	0.03	32	1
initial solution (mg L^{-1})	0.13	0.01	0.62	0.05

The adsorption capacity (q_t) was calculated according to equation 1.

$$q_t = (C_0 - C_t) V/m \quad (1)$$

where C_0 is the initial concentration of the solution (mg L^{-1}), C_t is the concentration in a given time (mg L^{-1}), V is the volume (L) and m is mass of the adsorbent (g).

Figure 1 shows the adsorption capacity and the percent of removal for cobalt ions as a function of the pH. It can be seen that both q_e and % of removal present low values below pH 8. Studies concerning Co adsorption in biomass have shown that the adsorption process is higher at pH 6 [10]. The results here observed must be related to the fact that the pH of the solution was adjusted and the *Eichhornia crassipes* root biomass was posteriorly added. Therefore, the pH during the adsorption experiment should have been lowered to values lower than the initial one.

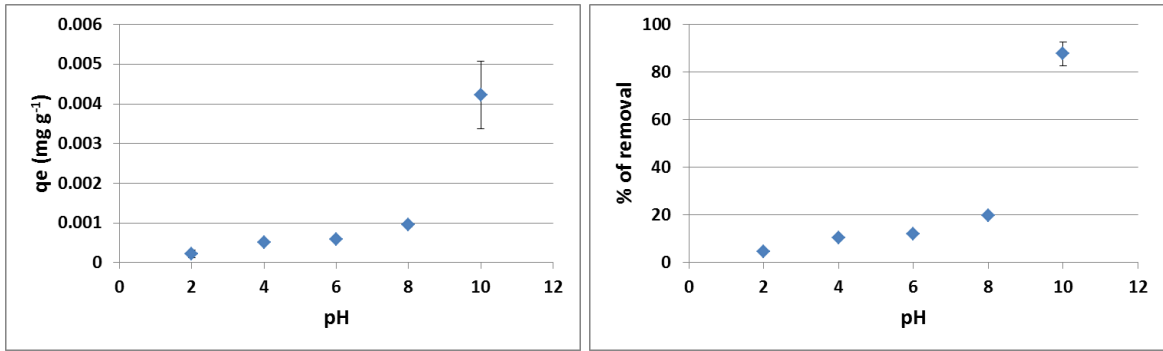


Figure 1: Adsorption capacity (q_e , mg g^{-1}) and percent of removal as a function of the pH for cobalt ion.

Figure 2 shows the adsorption capacity and the percent of removal for zinc ions as a function of pH. The q_e values showed the same behavior as that observed for cobalt. Nevertheless the % of removal, for this ion, was near 100% in all pH, indicating that the zinc adsorption is process independent of the solution pH.

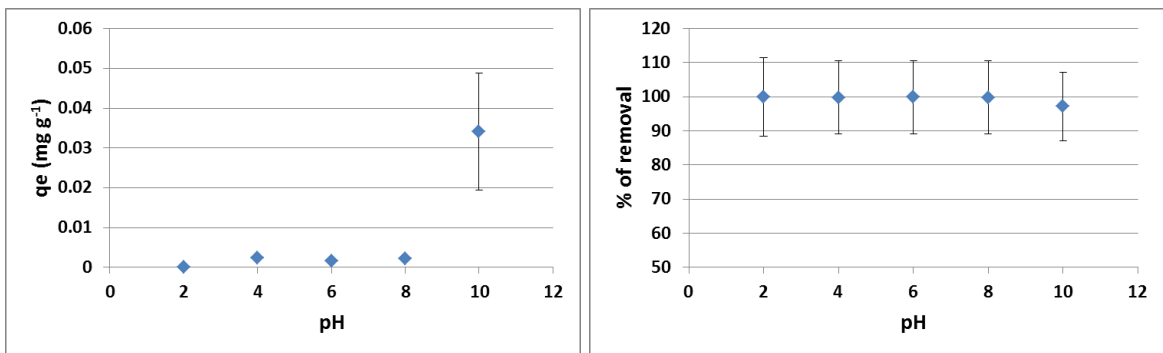


Figure 2: Adsorption capacity (q_e , mg g^{-1}) and percent of removal as a function of the pH for zinc ion.

For the contact time experiments, the pH was adjusted to 6 after the addition of the adsorbent in the solution. The adsorption capacity and the percent of removal for cobalt ions as a function of the contact time are showed Figure 3. Higher values of q_e and % of removal was observed at the initial times, lower than 30 min.

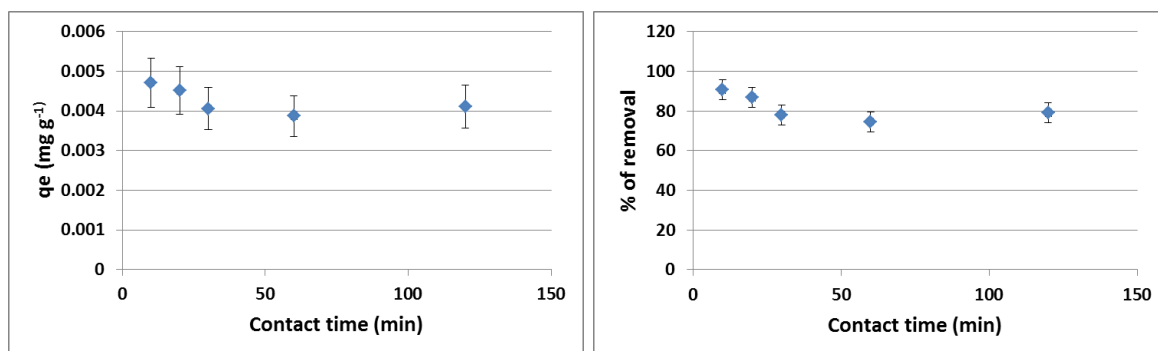


Figure 3: Adsorption capacity (q_e , mg g^{-1}) and percent of removal as a function of the time of contact for cobalt ion.

For the zinc ions removal as a function of the contact time, the results of q_e and % of removal are shown in Figure 4. As for Co ions, higher values were obtained before 30 min of contact time. Nevertheless, the percent of removal seen to decrease with time indicating that Zn adsorption was less dependent of the pH but more dependent of the contact time.

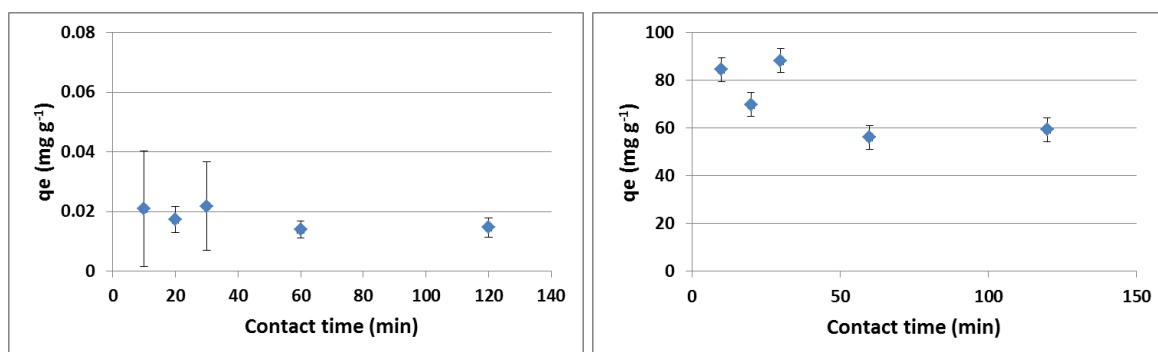


Figure 4: Adsorption capacity (q_e , mg g^{-1}) and percent of removal as a function of the time of contact for zinc ion.

4. CONCLUSIONS

In this study it was verified the influence of pH and contact time in the adsorption process of cobalt and zinc ions from aqueous solution by using biomass obtained from the acid activated roots of *Eichhornia crassipes*. Results indicated that the addition of the biomass to the solution cause a decrease in its pH. Therefore the pH of the solution must be adjusted to 6, optimized pH to adsorption of Co, after the addition of the biomass. In the case of Zn, the pH seems not to affect the adsorption process. The contact time for maximum removal of both ions was between 20 and 30 min.

ACKNOWLEDGMENTS

The authors thank CNEN for the grant of the master's degree.

REFERENCES

1. Q. Feng, Q. Lin, F. Gond, S. Sugita, M. Shoya, "Adsorption of lead and mercury by rice husk ash", *J. Colloid Interface Sci.* **278**, pp. 1–8 (2004).

2. M. Kylyc, C. Kyrbyyyk, O. Çepeliöullar, A.E. Pütün, “Adsorption of heavy metal ions from aqueous solutions by bio-char, a by-product of pyrolysis”, *Appl. Surf. Sci.* **283** pp. 856–862 (2013).
3. F. Fu, Q. Wang, “Removal of heavy metal ions from wastewaters: A review”, *Journal of Environmental Management*, **92** (3) pp. 407-418 (2011).
4. A. T. Ojedokun, O. S. Bello, “Sequestering heavy metals from wastewater using cow dung”, *Water Resources and Industry*, **13** pp. 7-13 (2016).
5. H. A. Hegazi, “Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents”, *HBRC Journal*, **9** (3), pp. 276-282 (2013).
6. M. J. Ahmed, “Application of raw and activated *Phragmites australis* as potential adsorbents for wastewater treatments”, *Ecological Engineering*, **102**, pp. 262-269 (2017).
7. N. Tahir, H. N. Bhatti, M. Iqbal, S. Noreen, “Biopolymers composites with peanut hull waste biomass and application for Crystal Violet adsorption”, *International Journal of Biological Macromolecules*, **94** (Part A), 210-220 (2017).
8. M. D. Meitei, M. N. V. Prasad, “Adsorption of Cu (II), Mn (II) and Zn (II) by *Spirodela polyrhiza* (L.) Schleiden: Equilibrium, kinetic and thermodynamic studies”, *Ecological Engineering*, **71**, pp. 308-317 (2014).
9. M. Zabihi, A. Ahmadpour, A. Haghghi Asl, “Removal of mercury from water by carbonaceous sorbents derived from walnut shell”, *Journal of Hazardous Materials*, **167**, (1–3), pp. 230-236 (2009).
10. R. Foroutan, H. Esmaili, S. D. Rishehri, F. Sadeghzadeh, S. Mirahmadi, M. Kosarifard, B. Ramavandi, “Zinc, nickel, and cobalt ions removal from aqueous solution and plating plant wastewater by modified *Aspergillus flavus* biomass: A dataset”, *Data in Brief*, **12**, pp. 485-492 (2017).