Using natural coal to treat and adsorb nickel ions from effluents

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Abstract: The development of low cost water treatment using adsorption process to treat and remove Ni (II) toxic ions from mining effluents using bamboo coal after pyrolysis. The adsorption experiments were performed using fixed-bed column and synthetic Ni (II) solution with concentration equivalent with those found in literature for mining effluents. The experimental results allow the kinetic calculations by linear regression and the comparison between the experimental results and adsorption models of Thomas, Yoon-Nelson, and Adams-Bohart. The experimental data were in agreement with Thomas and Yoon-Nelson models, in spite of Adams-Bohart model showed low correlation. The use of natural bamboo coal to adsorb and remove nickel ions from nickel solutions indicate 300min as saturation point curve and highlight a promising alternative to treat mining effluents using local and low cost material to concentrate toxic metals and possible secondary the water resource.

Keywords: nickel, mining effluent, vegetal coal, adsorption, adsorbent

Introduction

The global metals industry is now dealing with multifaceted challenges as it is required to deal with declining ore grades, meet more stringent environmental regulations and be more energy efficient, all while remaining cost competitive. Using a case study of the nickel industry, the climate change policies would influence the current mining industry operation and to evaluate their environmental sustainability including their potential to achieve co-benefits using the low concentration or as a future Nickel source, when the natural resources were not so abundant as today. A multi-criteria decision analysis model was used to simulate industrial decision making and future policy scenarios (Fukuzawa, 2012)

The mining environmental impact involving effluents with toxic metals are a constant reality, especially in mining countries like Brazil. In some locations both rural and urban areas have been used as mining activity dumping site. Nowadays government initiatives and environmental agencies are promoting more effective environmental control and regulation of mining activities. But still represent a long way to promote the mining sustainability and ensure the environmental safety avoiding, the toxic metal discharge in soil and surface water sources.

The Ni-rich ore shows many contaminants, with contents of Fe_2O_3 between 72.1 and 77.2% and contents of Ni between 1.6 and 2.1%, is probably derived from a peridotite bedrock containing, in addition to olivine, Ni-bearing orthopyroxenes. Peridotite containing Al-clinopyroxene might be, on the other hand, the parent rock of the Ni-poor ore, with Fe_2O_3 contents between 42.6 and 62.6% and Ni contents between 0.24 and 0.96% (Oliveira, 2001).

The most important nickel reserves in Brazil (for electrolytic nickel) are in the Federal State of Goiás with about 74% of total nickel production (300 million tons of reserves). The municipality of Niquelândia accounts for 37% of this total with two full operational mining units. Almost all of the extracted metal ore is transport and processed in the metallurgical units of the Federal State of São Paulo, producing about 23,000 tons of nickel per year.

In Brazil as in many countries with large mining activity, it is common the toxic metals presence as industrial waste which contaminates soil, groundwater, water supply for the population and surface water resources used for agriculture. Thus, it is urgent the development and the adoption of sustainable mining and economically viable water treatment practices responsible for toxic metals retention, for the environmental preservation, remediation and recovery the water from mining effluents (HO et al, 2002).

The toxic metal ions of nickel in human exposition results on acute dermatitis, consisting of itching of the fingers, hands, and forearms, related as the most common effect in humans from chronic (long-term) skin contact. Some respiratory effects have also been reported in humans from inhalation exposure to nickel. Human and animal studies have reported an increased risk of lung and nasal cancers from exposure to nickel refinery dusts and nickel subsulfide. Animal studies of soluble nickel compounds (i.e., nickel carbonyl) have reported lung tumors. EPA has classified nickel refinery dust and nickel subsulfide as possible human carcinogens, and nickel carbonyl as probable human carcinogen (EPA, 1999).

The Reference Dose (RfD) for nickel (soluble salts) is 0.02 milligrams per kilogram body weight per day (mg/kg/d) based on decreased body and organ weights in rats. The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer effects during a lifetime. At exposures increasingly greater than the RfD, the potential for adverse health effects increases. Lifetime exposure above the RfD does not imply that an adverse health effect would necessarily occur (EPA, 1999)

The adsorption is one of the most common and low cost water treatment techniques which presents metal pollutant retention and have been universally considered economically viable for the water treatment of large volumes including mining effluents(Ortiz, 2001). The current trend is focused on water safe and the integration of combined techniques and possibly promoting the use of lower cost materials as coal produced locally to promote the wastewater treatment and possibly provide a secondary water resource.

The use of natural coal produced locally to adsorb and remove metal ions from mining effluents is favorable as a local alternative to treat and reduce the presence of toxic metals in the environment (Ortiz, 2001 and Ahmad, 2010). The natural coal was chosen due its properties: high surface area, crystal structure with microchannel, large pores, nontoxicity and chemical stability. Those properties are very favorable for adsorption process development, mainly associated with the presence of hydroxyl surface charges. In addition, the saturated coal adsorbent can be treated using hydrolysis processes and regenerated to be reused in another cycle of wastewater treatment.

The analysis of adsorption processes using fixed-bed column data considering the maximum adsorption capacity (Q_T) of the adsorbent is calculated by Equation I:

$$Q_T = \frac{C_0 V}{1000\, m} \int_0^t (1 - C_t/C_0)dt \qquad \text{I}$$

Where: Q_T (mg/g) is maximum adsorption capacity of the adsorbent, V (mL/min) is flow rate, C_0 (mg/L) is the initial dye concentration, C_t (mg/L) is the Ni^{2+} concentration in specified time, and m (g) is mass of the adsorbent. The value of integral is the area under the breakthrough curve.

The total amount of Ni^{2+} sent to the column (W_{total}) is calculated from Equation (II) as follows:

$$W_{total} = \frac{C_0\, x\, V\, x\, t}{1000\, x\, m} \qquad \text{II}$$

The total amount of Ni^{2+} in percentage removed is the ratio of the maximum capacity of the column (Q_T) to the total amount of Ni^{2+} sent to the column (W_{total}) expressed as Equation III:

$$\%\, Removal = \frac{Q_T}{W_{total}} X\, 100 \qquad \text{III}$$

The column dynamic studies in the Adam's–Bohart model describe the relationship between (C_t/C_0) and time (Bohart and Adams, 1920). The Adams-Bohart model basically describes the initial part of the breakthrough curve and focus on some characteristic parameters such as the maximum adsorption capacity (N_0) and kinetic constant K_{AB}. The mathematical equation of the model can be written in Equation IV as:

$$\ln\left({}^{C_t}/_{C_0} \right) = K_{AB}\, C_0 t - K_{AB}\, N_0 \left({}^{Z}/_{F} \right) \qquad \text{IV}$$

Where: C_0 and C_t are the inlet and outlet adsorbate concentration, respectively (mg L^{-1}), Z is the bed height (cm), F is the superficial velocity (cm min^{-1}), N_0 is the saturation concentration (mg L^{-1}), and K_{AB} is the kinetic constant (L mg^{-1} min^{-1}). The last two values can be calculated from the intercept and slope of the plot of ln (C_t/C_0) against time (t).

The Thomas model is based on the assumption that the adsorption behaviour follows Langmuir kinetics and assumes that the rate driving forces obey the second order for reversible reaction kinetics (Thomas, 1944). The linearized form of the model is given in Equation V, as follows:

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{K_{Th}\,q_{Th}m}{Q}-k_{Th}\;C_o\,t \tag{V}$$

Where: K_{Th} is the Thomas rate constant (ml mg^{-1} min^{-1}), q_{tH} is the equilibrium adsorbate uptake (mg g^{-1}), W is the adsorbent amount in the column (g), and Q is the feed flow (ml min^{-1}), C_0 and C_t are the inlet and outlet adsorbate concentration, respectively (mg L^{-1}), The values of K_{Th} and q_{Th} can be calculated from the slope and intercept of the linear graph between $\ln(C_t/C_0-1)$ versus t at different inlet concentrations, flow rates, and bed heights.

The Yoon-Nelson model was a derivation based on the assumption that the adsoption rate decrease for each adsorbed adsorbate molecule and is proportional to the adsorption velocity and the adsorbate breakthrough the adsorbent (Yoon and Nelson, 1984). It is a simple model that requires no detailed data concerning the type of the adsorbent and the physical properties of the adsorption bed. The linearized model for a single component system is expressed as:

$$\ln\left(\frac{C_t}{C_0-C_t}\right)=K_{YN}\,t-\mathcal{T}K_{YN} \tag{VI}$$

Where: K_{YN} is the rate constant (min-1); $\mathcal{T}$ is the time required for 50% adsorbate breakthrough (min) C_0 and C_t are the inlet and outlet adsorbate concentration, respectively (mg L^{-1}), and t is the breakthrough time (min). The values of K_{YN} and $\mathcal{T}$ can be calculated from a plot of $\ln\ (C_t/C_0-Ct)$ versus t at different inlet concentrations, flow rates, and bed heights.

Methods

The bamboo coal used in the experiments was the residual fraction with small particle size obtained after pyrolysis process by Oficina Orgânica located in the municipality of Atibaia São Paulo State. The particle size analysis indicates the granulometric fraction with diameter < ASTM 100 mesh to be used due the high surface area of 200 m^3 / cm^2. The collected samples after pyrolysis were analyzed by scanning electron microscopy SEM (morphology), the micrography can be observed on Figure 1.

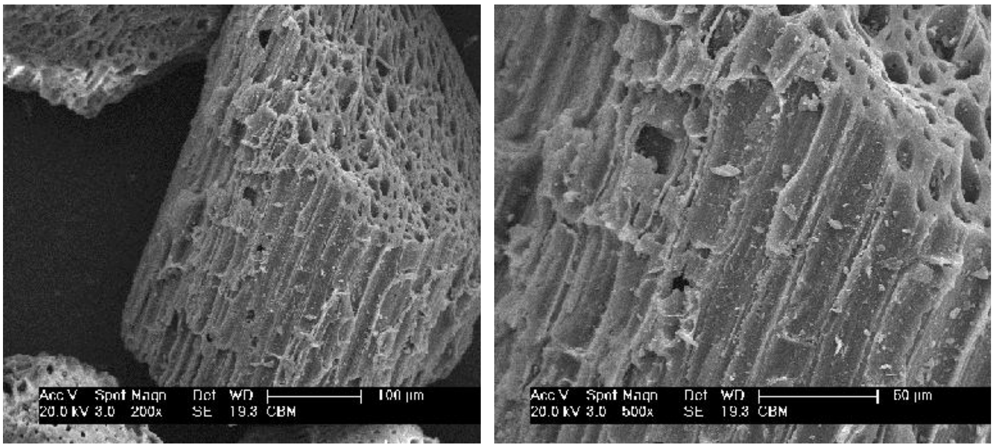

Figure 1: SEM micrography of bamboo coal with magnification of 200x (left) and 500x (right).

The coal micrography clear show the tubular structure, elevate number of pores and high surface area. Those properties are very favorable for the development of adsorption processes.

The adsorption process was used in batch system and fixed –bed adsorption columns. Fixed bed adsorption column with 2 g and 5.5 cm height of bamboo coal were used at room temperature (24oC) and constant flow rate of 2.5 mL per minute for the elution of the nickel synthetic solution with concentration of 2 mg L^{-1}. The aliquots were collected on different elution time intervals: 30, 60, 90, 120, 180, 240, 300, 360 min. After elution all collected aliquots were measures for nickel ions concentration.

The experiments conducted in batch were performed with controlled temperature under constant agitation, using 2 g of natural coal added to 500 mL of synthetic nickel solution with 2 mg L^{-1}as stock solution, diluted accordingly with the needed nickel initial concentration. The nickel aliquots were collected in different mixture time intervals or percolation time for fixed bed experiments: 30, 60, 90, 120, 180 e 240 min. The nickel concentrations were in all collected aliquots after centrifugation of 15 min at 15000 rpm. The supernatant of all aliquots in both systems were collected and measured using the Inductively Coupled Plasma- Optical Spectrometry Spectroflame M120 E after calibration curve prepared with nickel standards solutions.

Results

The Figure 2 presents the normalized curve obtained using the Nickel concentration (C_t/ C_o) versus percolation time for 2.0 mg Ni/L and bamboo coal column at pH=5. The curve will be referred to as breakthrough curve and was defined at C_t=0.05 C_o. The adsorption column parameters were reported in Table 1. The breakthrough time occurred after 23 min.

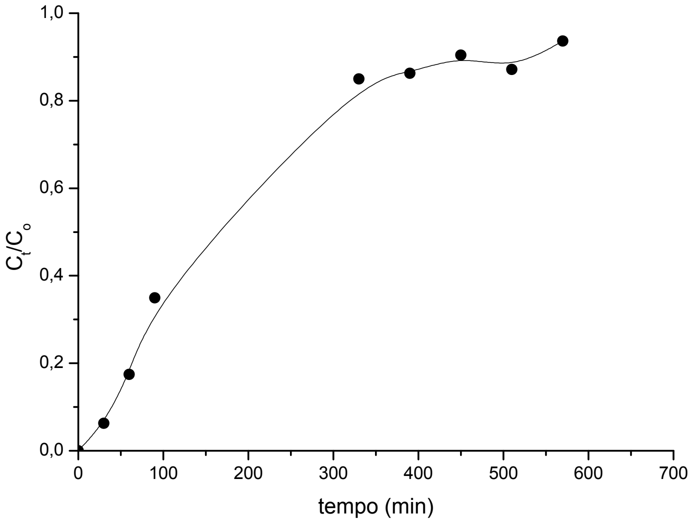

Figure 2. Breakthrough curves for 2.0 mg/L Ni(II) adsorption on bamboo coal (bed height = 5.5 cm, flow rate = 2.5 mL min^{-1}, pH 5, temperature= 25 ±1◦C)

Table 1. Adsorption column parameters from the breakthrough curve to Ni(II) adsorption on bamboo coal.

Parameter	**Value**
t_b (min)	23
t_e (min)	570
V_e (mL)	1425
% R	35.1
Q_T (mg/g)	5.0 x 10^{-4}

Where: t_b = breakthrough time (C_t/C_o ~0,05); t_e = saturation time (C/C_o ~0,95); V_e = total volume of wastewater treated to the point of exhaustion

The Thomas, Yoon-Nelson and Adams-Bohart parameters were evaluated using linear regression analysis for Ni (II) adsorption on fixed-bed. The results and correlation coefficient (R^2) of kinetic models are presented in Figures 3, 4, 5 and Table 2.

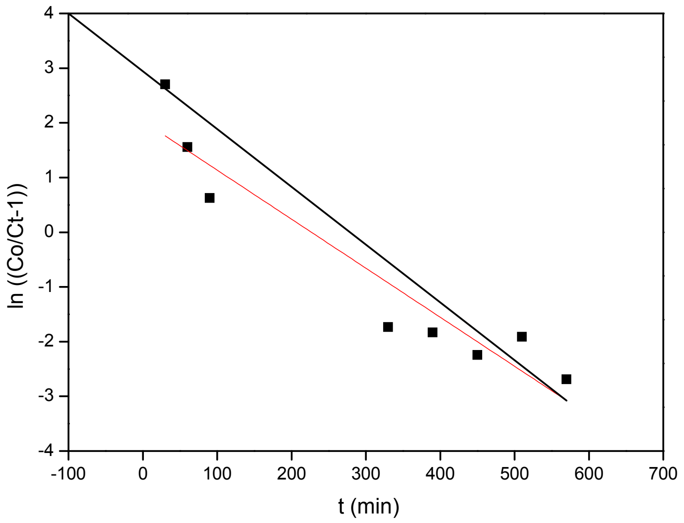

Figure 3. Linear plot of Thomas model for Ni(II) on bamboo coal

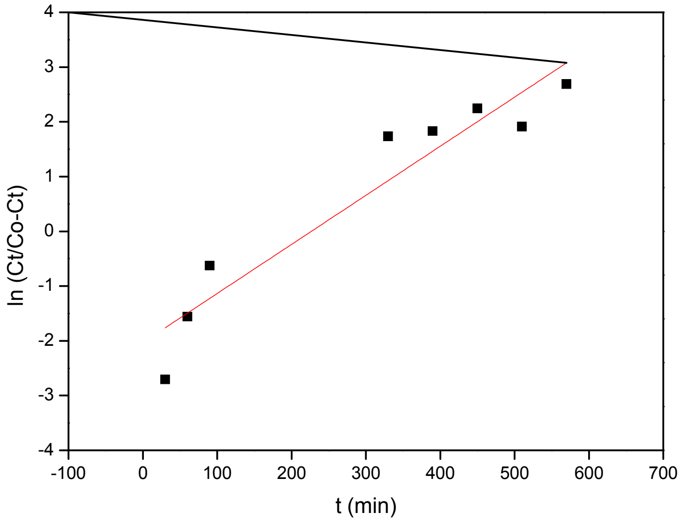

Figure 4. Linear plot of Yoon-Nelson model for Ni(II) on bamboo coal

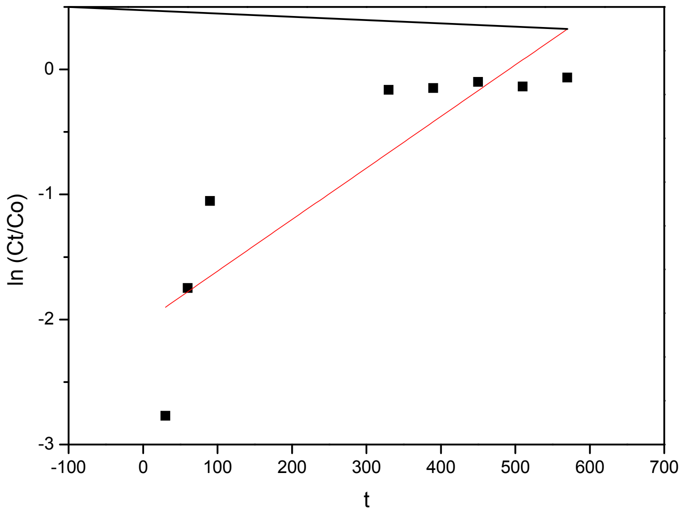

Figure 5: Linear plot of Adams-Bohart model for Ni(II) on bamboo coal

Figure 3, 4 and 5 and Table 2 show the adsorption parameters and the better agreement with Thomas and Yoon-Nelson models. They are more appropriate to describe Ni adsorption on fixed-bed system. In spite of that the Adams-Bohart model shows the lower correspondence (R^2 =0.877) which indicate Adams-Bohart model cannot be a predictor for the breakthrough curve behavior.

Table 2: Thomas, Yoon-Nelson and Adams-Bohart models parameters using linear regression analysis for Ni(II) on bamboo coal

Model Type	**Parameter**
Thomas	
k_{Th} (L min^{-1} mg^{-1})	4.48 x 10^{-3}
q_o (mg g^{-1})	0.567
R^2	0.953
Yoon-Nelson	
K_{YN} (min^{-1})	2.03
ʊ (min)	226.8
R^2	0.953
Adams-Bohart	
k_{AB} (L mg^{-1} min^{-1})	2.05 x 10^{-3}
N_o (mg L^{-1})	63.7
R^2	0.877

The experimental results in batch systems indicate an adsorption process favorable for nickel ions remove using natural coal and adsorption fixed bed columns. The batch systems shows 86 % of removal percentage at 17oC and the adsorption column the saturation point were observed after 300 min with flow rate of 2.5 mL min^{-1} and nickel concentration of 2mg L^{-1} , Figure 6.

The adsorption process result on 1mg of nickel ions using 2g of natural coal and the production of 500mL of available water source. Described in literature, usually the nickel mining effluents shows less than 2mg L^{-1} and have also others competitor contaminant for the adsorption sites. Considering this possibility the adsorption process have to be adapted accordingly with each effluent composition. It is also recommended the study of nickel degradation by microorganisms, especially in the natural coal recuperation and reutilization steps.

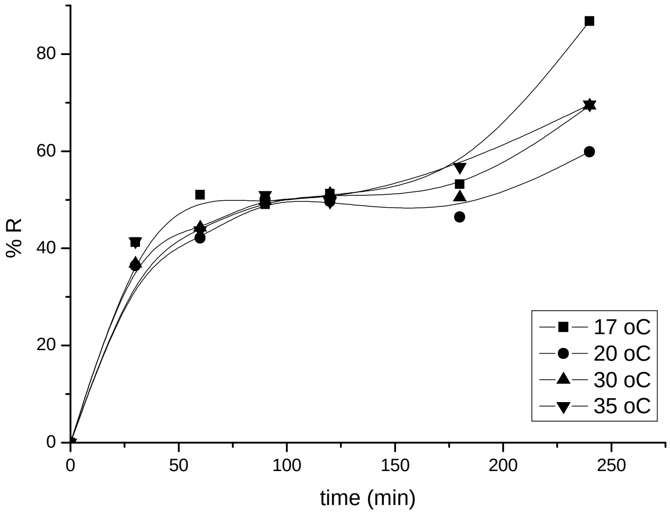

Figure 6: Nickel removal percentage on different mixture time and temperatures

Conclusions

The use of bamboo coal after pyrolysis to adsorb and remove nickel ions from mining effluents shows promising perspectives. A low cost and on site adsorbent product to be used to treat, remove and produce water secondary water resource from mining effluents combined with the possible use of microrganisms to nickel ions degradation and natural coal reutilization. From this study, bamboo coal was found suitable for Ni(II) removal from aqueous solution using batch adsorption process with 86 % of removal percentage at 17oC. The comparison between Thomas, Yoon-Nelson, and Adams-Bohart kinetic models with experimental data was performed, and model parameters were determined by linear regression analysis for Ni (II) adsorption. The column experimental data were in agreement with Thomas and Yoon-Nelson models, but the Adams-Bohart model predicted poor performance of fixed-bed column behavior.

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