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# *Agave salmiana* as biosorbent of cobalt and cobalt-nickel ionic species from aqueous solutions

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## ABSTRACT

The *Agave salmiana* biosorption behavior for cobalt ions ($Co^{2+}$) and cobalt-nickel ions ($Co^{2+}$-$Ni^{2+}$) from aqueous solutions have been investigated in this study. The removal of Co(II) and Co(II)-Ni(II) was evaluated in a batch system as a function of contact time, pH, and the initial concentration of each metal in the solutions. It was observed that the biosorption equilibrium was reached after 60 min in all cases: Co(II) from a monocomponent solution and Co(II) and Ni(II) from a bicomponent solution. Pseudo-first-order and pseudo-second-order models were applied to the kinetic sorption process. The experimental data were well described by the pseudo-second-order model in all cases. The pH range observed for the maximum biosorption by *Agave salmiana* for the removal of $Co^{2+}$ and $Co^{2+}$-$Ni^{2+}$ from aqueous solutions was between 6 and 10. The maximum biosorption capacity ($q_{max}$) of the *Agave salmiana* for Co(II) with the base on the Langmuir model was 6.69 mg Co/g *Agave*. However, the uptake data for Co(II) and Ni(II) from bicomponent solution was described well by a linear model, and the sorption capacities were 50.02 mg Co(Co-Ni)/g *Agave* and 57.7 mg Ni(Co-Ni)/g *Agave*. The $K_d$ value was higher for Ni(II)(Co-Ni) than for Co(II)(Co-Ni). These results showed that *Agave salmiana* exhibits a notable difference in the sorption capacity of the biosorbent when Co was presented in the bicomponent solution compared to that of monocomponent solution. The adsorption capacity for Ni(II) is higher for Co(II) in a bicomponent solution. The metals' co-precipitation could play a role in the biosorption processes.

*Keywords: Agave salmiana*; Biosorption; Cobalt; Cobalt-nickel solution

## 1. Introduction

The pollution of water by heavy metals is a problem that causes big concern around the world. Inorganic micropollutants are non-biodegradable, highly toxic and have carcinogenic effect [1]. Cobalt and nickel, by their toxicity, are part of this problem.

In the periodic table, nickel and cobalt are elements of transition group VIIIB of the 4th period. Nickel with atomic number 28 and cobalt 27, practically shows similar electronic configuration. In nature, the existence of these two metals are always found together. In the production of nickel ore involve the presence of a mixture of cobalt metal alloys. Thus, these two metals are found together in polluted waters [2]. Furthermore, cobalt is present in the wastewater of nuclear power plants [3] and many other industries such as mining, metallurgical, electroplating, paints, pigments, and electronic industries [4]. These heavy metals

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present a high health risk when they enter the human food chain [5,6]. Exposure to nickel and cobalt can produce anemia, liver and kidney diseases, brain damage and causes death. High levels of cobalt cause health problems such as paralysis, diarrhea, low blood pressure, lung irritation and bone defects [7,8]. According to WHO, the limit of cobalt in drinking water is 0.005 mg/L and for nickel is 0.02 mg/L [9].

These heavy metals must be removed from wastewater before being discharged into water bodies as it causes damage to environment and pose a risk to human health.

Adsorption of cobalt and nickel ions by different types of biomaterials has been the subject of several research [10–12]. In these studies, researchers investigated the effect of different factors that affect the adsorption process such as sorbent amount, initial metal-ion concentration, contact time and pH solution. The non-living biomasses used in these researches were *Pinus caribaea*, Morelet sawdust, coconut, and marine macroalgae.

The genus *Agave* is one of the most diverse and rich groups of plants in Mexico. In this country, the people have developed several technologies to extract products from *Agave*, and for many years they have consumed different alcoholic beverages derived from this plant: Tequila, Mezcal, and Pulque among others [13,14]. The potential production of *Agave* for 2024 is estimated at 1,926.42 thousand tons [15]. Therefore, agricultural wastes that are generated from the *Agave* industrialization can be used to separate heavy metals from water as other kinds of biomasses [16,17]. Moreover, the adsorptive properties of *Agave* can be improved with treatments or modifications that include basic or acid solutions, mineral, and organic acid solutions [18]. For this reason, it is important to investigate the biosorption properties of this plant to remove heavy metals from water. Therefore, this work aimed to describe the adsorption behavior of modified *Agave salmiana* to remove Co(II), Co(II)(Co-Ni), and Ni(II)(Co-Ni) from mono and bicomponent aqueous solutions considering the contact time, the pH, and the concentration of Co and Ni. It is important to mention that the originality of the manuscript was the description of the sorption behavior of Co from mono and bicomponent system where Ni is present in solution and acid-modified *Agave salmiana* as biosorbent.

## 2. Experimental

### 2.1. Biomaterial

The preparation of *Agave salmiana* from San Jerónimo Acazulco (Mexico) washed with distilled water, named AS-N; and treated with a $10^{-4}$ M HCl solution, represented as AS-H, and its characterization were previously reported [18] and considered in this study. The pH of the zero charge point of AS-H was close to neutrality ($pH_{pzc} = 7.4$) and the specific area for AS-N and AS-H were 0.7954 and 1.084 $m^2/g$, respectively. It is important to mention that the AS-H specific surface area is 1.36 times higher than that of AS-N and it could influence the Co(II) and Ni(II) adsorption processes. The *Agave salmiana* is fundamentally an amorphous material. However, crystalline structures were identified as calcium oxalate and calcite was observed in the XRD patterns. Additionally, carboxyl, hydroxyl, and nitrogen groups were presented in the biomass according to the FTIR analysis reported by Sánchez-Nava *et al.* [18].

### 2.2. Preparation of Co(II) and Co(II)-Ni(II) aqueous solutions

The Ni(II) removal from aqueous solutions by *Agave salmiana* was previously published. However, for comparison, the results obtained from that work was mentioned [18].

A stock solution of Co ($CoCl_2·6H_2O$, analytical grade reagent from Merck) was prepared with distilled water. The concentration of this solution was 600 mg $L^{-1}$. The Co(II)-Ni(II) bicomponent system (1:1) was prepared as a part of the Co(II) solution and a part of the Ni(II) solution with the same concentration. The concentrations of cobalt and nickel from the mono and bicomponent solutions, Co(II) and Co(II)-Ni(II), before and after adsorption by AS-H, were determined using an atomic absorption spectrophotometer model GBS 932 Plus with a wavelength at 240.7 nm for cobalt and 232.0 nm for nickel, considering a calibration curve from 2.5 to 8 mg/L for cobalt and 0.25 to 5 mg/L for nickel, respectively.

### 2.3. Uptake of Co(II) and Co(II)-Ni(II) from aqueous solutions

Batch experiments were carried out at 293 K to determine the uptake kinetics by shaking closed vials from 5 min to 24 h with a mixture of 100 mg of AS-H and aliquots of 10 mL of a 25 ppm Co(II) solution at pH 5.5. The Co(II)-Ni(II) bicomponent system was 5 mL of the Co(II) solution and 5 mL of the Ni(II) solution with the same concentration (25 ppm). A Cole Parmer Polystat, model 12050-00 temperature circulator bath was used for these experiments. The residual cobalt from monocomponent solutions and Co(II)-Ni(II) from bicomponent solutions after the sorption by AS-H were then filtered to separate the phases, to each other. The supernatant liquid was recovered and analyzed.

To determine the effect of the pH on the sorption of the ionic species ($Co^{2+}$ and $Co^{2+}$-$Ni^{2+}$) by AS-H both solutions of 25 mg $L^{-1}$ at 293K were performed to adjusted pH values from 2 to 12. The adsorption isotherms of the Co(II) and Co(II)-Ni(II) from aqueous solutions were obtained with different concentrations of the metallic species from 5 to 600 mg/L during 24 h of contact time considering a pH value of 5.5 and 293 K of temperature. The concentration of Co and Ni were determined as was described before. All experiments were carried out in duplicate.

The amount of Co(II) and Ni(II) from mono- and bi-component solutions per unit mass of the sorbent and the corresponding percentage of each of them were calculated as follows:

$$q_e = \frac{\left(C_0 - C_e\right)}{m} V \tag{1}$$

$$R = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{2}$$

where in Eq. (1) $q_e$ (mg $g^{-1}$) is the amount of Co(II) and Ni(II) from mono and bicomponent solutions adsorbed by AS-H,

$C_0$ and $C_e$ are the initial and equilibrium Co(II) and Ni(II) concentrations in solution (mg $L^{-1}$) at any time, respectively. $V$ is the volume of solution (L), and $m$ is the amount of adsorbent (g). In Eq. (2), $R$ represents the percentage of Co(II) or Ni(II) from mono and bicomponent solutions by AS-H, considering the values of $C_0$ and $C_e$ described before.

## 3. Results and discussion

### 3.1. Uptake of Co(II) from mono and bicomponent solutions

#### 3.1.1. Sorption kinetics of Co(II) from mono and bicomponent solutions

Fig. 1 shows the Co(II), and Co(II)(Co-Ni), Ni(II)(Co-Ni) uptake from mono and bicomponent solutions by AS-H as a function of time. It can be seen that the biosorption of the metallic species by acid-modified *Agave salmiana* was in two steps. In the first step, a fast Co(II), Co(II)(Co-Ni), and Ni(II)(Co-Ni) uptake were found. However, in the second step, a plateau after 60 min was observed, indicating that the equilibrium of the sorption process was reached in all cases, Co(II), Co(II)(Co-Ni), and Ni(II)(Co-Ni).

Table 1 shows the results of the adsorption and the removal percentage of Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni) at 300 min. In all cases, the removal percentage was high than 75%. It is important to note that the presence of Ni(II) in the bicomponent solution affect the sorption of Co(II) comparing to the results obtained for Co(II) from monocomponent solution.

According to the results by Sánchez-Nava et al. [18], the sorption for Ni(II) by AS-H is similar with respect to that found for Co(II) (2.04 mg/g) from monocomponent solutions. This behavior is different for Ni(II) (2.17 mg/g) which is slightly higher adsorbed by the same biomass than the Co(II) (1.90 mg/g) from bicomponent solution (Table 1).

The sorption of the metallic ion by AS-H presents in the following order: Ni(II)(Co-Ni) > Co(II) > Co(II)(Co-Ni).

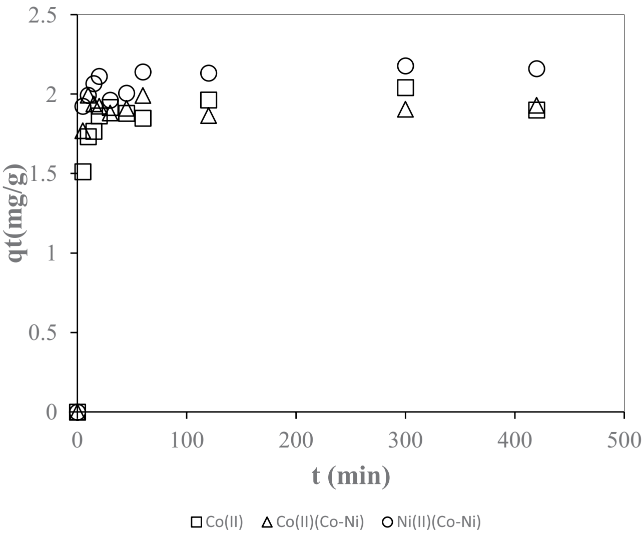

Fig. 1. Effect of contact time on Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni) sorption by the AS-H.

The experimental results were fitted to the second-order model to describe the sorption kinetic of Co(II) and Ni(II) from mono and bicomponent solutions by *Agave salmiana*. This model has been applied to describe the adsorption kinetics of heavy metals by other types of biosorbents [19].

The pseudo-second-order kinetic model [20] has generally been considered for heterogeneous surfaces where the sorption mechanism is attributed to chemical sorption and is generally expressed as:

$$\frac{dq_t}{d_t} = k\left(q_e - q_t\right)^2 \tag{3}$$

where $k$ is the rate constant of sorption (g $mg^{-1}$ $min^{-1}$), $q_e$ is the amount of solute sorbed at equilibrium (mg $g^{-1}$) and $q_t$ is the amount of solute sorbed on the time $t$ (mg $g^{-1}$). After integration and applying boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the equation is:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{4}$$

Figs. 2 and 3 shows that the sorption experimental data fitted well ($R^2 > 0.99$) to the pseudo-second-order kinetic model for all systems, Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni) considering the AS-H as a biosorbent.

The values of pseudo-second-order rate constants ($k_2$) and the sorption at equilibrium ($q_e$) are shown in Table 2.

The behavior of Co(II) sorption by AS-H from monocomponent solution is similar to that found by Ni(II) sorption by the same biomass from monocomponent solution. The pseudo-second-order equation and the parameters found by Sánchez-Nava *et al.* [18] for Ni(II) were: $y = 0.4616x + 2.8221$, $R^2 = 1$, $q_e = 2.17$ mg/g, and $k_2 = 0.07550$ g/mg min. It is important to mention that $k_2$ for Co(II) is 9.7 times higher than for Ni(II).

The sorption capacity ($q_e$) of the Co(II) from monocomponent system is slightly higher to that for Co(II) from Co-Ni bicomponent system. However, the $k_2$ is 2.46 higher for Co(II) in a bicomponent system than monocomponent system. The $q_e$ (2.17 mg/g) for Ni(II) [18] from monocomponent system was similar to those found for Ni(II) from Co-Ni bicomponent system, although the $k_2$ was higher for Ni(II) from the monocomponent system. The difference in the sorption capacities at equilibrium between Co(II) and Ni(II) as well as the differences in the pseudo-second-order kinetic constants, may be due to the Ni(II) has slightly more affinity by *Agave Salmiana*, when this element is in a bicomponent system and competes with Co(II) for the sorption sites of the biomass. By the other hand the Co(II)

Table 1
Adsorption and removal percentage of Co(II), Co(II)(Co-Ni), and Ni(II)(Co-Ni) at equilibration time of 300 min using AS-H

| Metals | Sorption at equilibrium (mg/g) | Removal (%) |
|---|---|---|
| Co(II) | 2.04 | 81.6 |
| Co(II)(Co-Ni) | 1.90 | 76.2 |
| Ni(II)(Co-Ni) | 2.17 | 87.1 |

Table 2
Pseudo-second-order kinetic parameters to describe the sorption kinetic of Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni) by AS-H from mono- and bicomponent solutions

| System | Equation | $q_e$ (mg/g) | $k_2$ (g/mg min) | $R^2$ |
|---|---|---|---|---|
| Co(II) | $y = 0.513x + 0.3563$ | 1.9493 | 0.7386 | 0.9983 |
| Co(II)(Co-Ni) | $y = 0.5205x + 0.1491$ | 1.9212 | 1.8170 | 0.9999 |
| Ni(II)(Co-Ni) | $y = 0.4599x + 0.7007$ | 2.1743 | 0.3018 | 0.9999 |

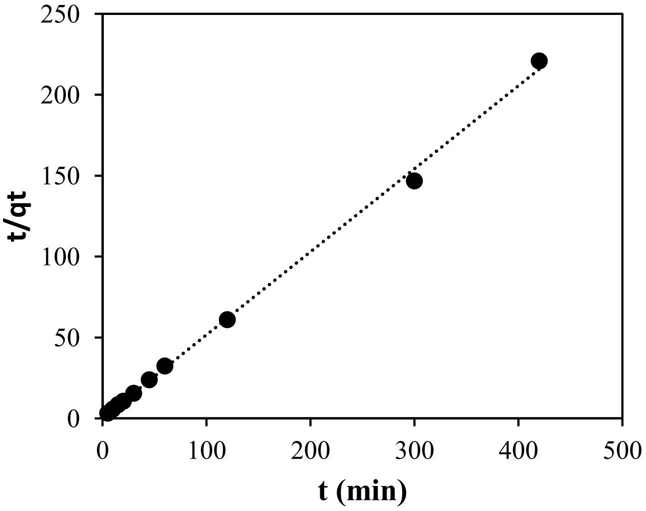

Fig. 2. Pseudo-second-order kinetic model applied to the sorption of Co(II) by AS-H from monocomponent solution.

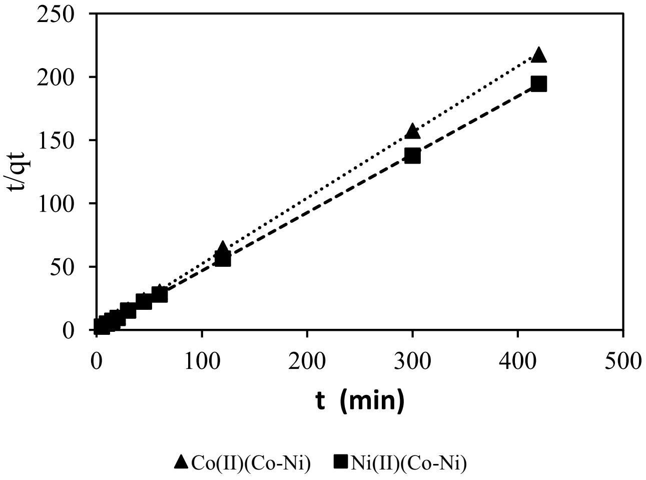

Fig. 3. Pseudo-second-order kinetic model applied to the sorption of Co(II) and Ni(II) by AS-H from bicomponent solution (Co-Ni).

reaches the adsorption sites in minor time than Ni(II). Furthermore, this behavior could depend to the physico-chemical properties of each cationic species. Both the $Co^{2+}$ and $Ni^{2+}$ have an ionic radii of 70 pm and electronegativity of 1.88 and 1.91 according to the Pauling scale.

Based on the results, the chemisorption could play an important role in the biosorption kinetic process of Co(II) and Ni(II) by AS-H from mono- and bicomponent aqueous solutions The pore volume and the size of the pore of this biomass could be play a role favoring the interaction and diffusion of the heavy metals to rich the specific sorption sites.

The pseudo-second-order model is commonly applied to heterogeneous materials. According to the determination coefficients obtained, the model that best describes the kinetic adsorption behavior of Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni) by AS-H is the pseudo-second-order model. According to Ho and McKay [20] the pseudo-second-order model indicates that the adsorption process can be chemisorption by ion exchange or by the formation of adsorbent/adsorbate bonds.

### 3.2. pH effect

Fig. 4 shows the Co(II) and Ni(II) uptake by AS-H from mono and bicomponent systems as a function of the pH. Clear difference was observed for the uptake of Co(II) from monocomponent system in comparison with the bicomponent system Co(II)(Co-Ni) as can be observed in Fig. 4. Therefore, the Ni(II) influence on the uptake of Co(II) at different pH values. The lower uptake of Co(II) and Ni(II) by the biomass was found at pH 2. It is important to mention that the $pH_{pzc}$ of the AS-H was 7.2, this means that the surface has a positive charge below this pH and the $Co^{2+}$ and $Ni^{2+}$ are present in the solution, therefore it is expected a coulombic repulsion. However, at acidic pH the $H^+$ could play a role in the adsorption process. When the pH is up to the $pH_{pzc}$ the surface has a negative charge and the cationic species could be biosorbed.

The maximum adsorption capacity of Co and Ni by *Agave salmiana* was observed at pH 10. The adsorption capacity following the order with respect to the pH 10: Co(II) > Ni(II) (Co-Ni) > Co(II)(Co-Ni) (Table 3). It is important to mention that the differences are smaller in all cases.

At pH 2 the adsorption capacity of AS-H is the lowest for Co(II) (0.37 mg/g), Ni(II) (0.07 mg/g) [18], Co(II)(Co-Ni) (1.12 mg/g), and Ni(II)(Co-Ni) (1.40 mg/g). The difference of 1.33 mg/g is observed in the uptake values between Ni(II)(Co-Ni) and Ni(II) and 0.75 between Co(II) and the Co(II)(Co-Ni), which these differences are lower at pH 10 (0.0073 and 0.2731 for Ni(II) and Co(II) respectively). This difference may be due to the presence of the chemical species of cobalt(II), nickel(II) in the bicomponent system and their affinity by *Agave Salmiana* biosorption sites.

It is important take in mind that Co(II) and Ni(II) exist mainly (99.5%) as $Co(OH)_2$ and $Ni(OH)_2$ at pH 10 . The cations $Co^{2+}$ and $Ni^{2+}$ are present at pH values < 2.0. In the pH

Table 3
Biosorption capacity and removal percentage of Co(II), Co(II)(Co(II)-Ni(II)), and Ni(II)(Co(II)-Ni(II)) bicomponent at pH 10

| System | Biosorption (mg/g) | Removal (%) |
|---|---|---|
| Co(II) | 2.55 | 99.11 |
| Co(II)(Co-Ni) | 2.28 | 89.89 |
| Ni(II)(Co-Ni) | 2.434 | 89.22 |

range from 5 to 10, $Co(OH)^+$, $Ni(OH)^+$, $Co(OH)_2$, $Ni(OH)_2$, $Co_2OH^{3+}$, can coexist in various proportions, and from pH values from 10 to 12, the species; $Co(OH)_2$, $Ni(OH)_2$, $Ni(OH)_3^-$ and $Co(OH)_3^-$ can be observed in solution. The cations and anions are the chemical species that may be sorbed on the biosorption sites from the *Agave salmiana* (AS-H).

The mechanism to explain the Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni) sorption by *Agave salmiana* at basic pH values could be through the oxygen containing groups (e.g., carboxylic and phenolic) from AS-H [21]. At basic pH value, the predominant species of Co(II) and Ni are $Co(OH)_2$, $Ni(OH)_2$, $Co(OH)^+$, and $Ni(OH)^+$. Then, it is possible that Co(II) and Ni(II) could be precipitated on the surface of AS-H or stablishing an interaction by difference of charge on the surface of the biomass.

$$2\left(\equiv R-\mathrm{COO}^-\right)+\mathrm{Co}^{2+}\leftrightarrow\left(\equiv R-\mathrm{COO}\right)_2\mathrm{Co} \tag{5}$$

$$\equiv R-\mathrm{COO}^-+\mathrm{Co}\left(\mathrm{OH}\right)^+\leftrightarrow\equiv R-\mathrm{COOCoOH} \tag{6}$$

$$\equiv R-\mathrm{COOH}+\mathrm{Co}\left(\mathrm{OH}\right)_2\leftrightarrow\equiv R-\mathrm{COOH}-\mathrm{Co}\left(\mathrm{OH}\right)_2 \tag{7}$$

$$4\left(\equiv R-\mathrm{COO}^-\right)+\mathrm{Co}^{2+}+\mathrm{Ni}^{2+}\leftrightarrow\left(\equiv R-\mathrm{COO}\right)_2\mathrm{Co}+\left(\equiv R-\mathrm{COO}\right)_2\mathrm{Ni} \tag{8}$$

The pH was measured in the solutions before and after the Ni(II) sorption process and the pH variation was low.

### 3.3. Sorption isotherms

It was observed that the sorption of Co(II) from monocomponent system is described by a Langmuir isotherm (Fig. 5). In this case the parameters obtained were $q_{\max}$ = 6.69 mg/g and a $K_L$ of 0.03259 which showed the affinity of Co by AS-H biomass.

The uptake behavior of Co(II) was similar to that found for Ni(II) from a bicomponent system (Co-Ni) (Fig. 6). In both cases, a linear model describe those isotherms due to the adsorption capacity increased continuously and the saturation of the *Agave salmiana* with the sorbed Co(II) or Ni(II) from (Co-Ni) system were not observed and this result could be due to the formation of metallic chemical species precipitated on the surface of the biomass when Co(II) and Ni(II) are present in same aqueous solution. The experimental data were fitted to Linear model and the distribution coefficients ($K_d$) showed that Ni(II) is preferentially adsorbed by Co(II). For Ni(II)(Co-Ni) was $K_d$ = 0.1533 L/g and for Co(II)(Co-Ni) 0.0974 L/g.

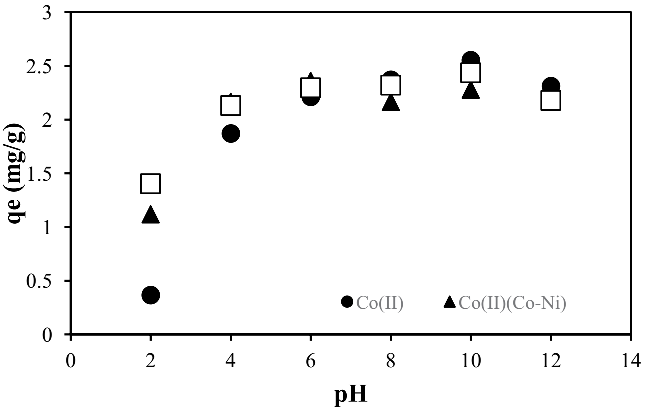

Fig. 4. Effect of pH on Co(II), Co(II)(Co-Ni), and Ni(II)(Co-Ni) biosorption by AS-H.

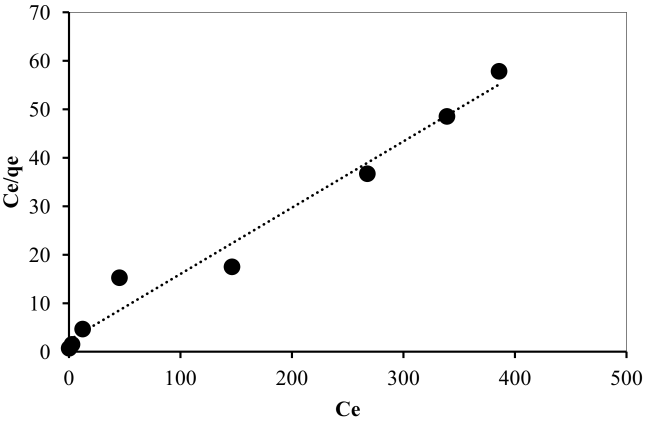

Fig. 5. Langmuir isotherm model applied to Co(II) biosorption from monocomponent aqueous solution by AS-H.

These results showed that the biosorbent *Agave salmiana* exhibits preference (affinity) in the sorption of Ni(II) over Co(II). There is also a competition for both metals Ni(II) and Co(II) to reach equilibrium when they are present in a bicomponent solution and the size of Ni(II) (1.21 Å) and Co(II) (1.26 Å) also could influence, as mentioned previously.

## 4. Conclusions

The sorption ($q_e$) of AS-H for Co(II) and Co(II)(Co-Ni) were similar and for Ni(II)(Co-Ni) was slightly high. The biosorption equilibrium was reached after 60 min in all cases, for instance, Co(II) from monocomponent solution, and Co(II)(Co-Ni) and Ni(II)(Co-Ni) from bicomponent solution. The pseudo-second-order model describes well the sorption kinetic behavior for Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni). The $k_2$ is affected by type of the system (monocomponent solution or bicomponent solution) and by the type of species involve (Co or Ni) in the sorption by AS-H as a function of time. The kinetic constant $k_2$ follows the order: $k_2$Co(II)(Co-Ni) > $k_2$Co(II) > $k_2$Ni(II)(Co-Ni).

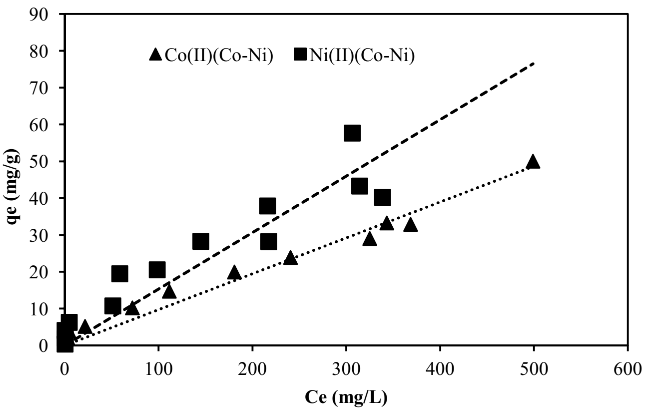

Fig. 6. Linear model applied to Co(II)(Co-Ni) and Ni(II)(Co-Ni) biosorption from bicomponent (Co-Ni) aqueous solution by AS-H.

The acid media does not promote sorption of Co or Ni efficiently from mono and bicomponent systems. The biosorbent (AS-H) mostly removes the Co(II), Co(II)(Co-Ni) and Ni(II)(Co-Ni) from the aqueous medium at pH 10.

The sorption isotherm experimental data of Co(II) from monocomponent aqueous solution by AS-H fits well to Langmuir model. For the cases of Co(II) and Ni(II) from bicomponent solution the experimental data are described by a linear model. The AS-H presents the highest capacity for Ni(II)(Co-Ni). The biosorbent exhibits preference (affinity) in the sorption of Ni(II) over Co(II). The distribution coefficient $K_d$ for Ni(II)(Co-Ni) is 1.57 higher than for Co(II)(Co-Ni).

This research demonstrated that the plant could be used as a biosorbent to remove Ni(II) and Co(II) from monocomponent and bicomponent solutions using, for instance, acid-treated *Agave salmania*.

## Conflict of interest

The authors have no conflicts of interest to declare.

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