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### Study of Calcium(II), Copper(II), Magnesium(II), and Iron(III) Interference on Au(III) Binding to Native Hop Biomass Using ICP-OES

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## Study of Calcium(II), Copper(II), Magnesium(II), and Iron(III) Interference on Au(III) Binding to Native Hop Biomass Using ICP-OES

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### ABSTRACT

Biosorption of metals from industrial effluents has been studied widely. The economic advantage of scavenging precious metals such as gold has increased the interest in recovery technologies. Hop biomass has been studied for its capability of uptaking Au(III) ions from aqueous solutions. The interference of Cu(II), Fe(III), Ca(II), and Mg(II) on Au(III) binding to hop biomass was studied using ICP-OES for metal quantification. Portions of hop biomass were reacted with mixed solutions of Cu(II)–Au(III), Fe(III)–Au(III), Cu(II)–Au(III), and Mg(II)–Au(III) at different

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concentrations. The analysis of the Cu(II)–Au(III) solution showed that Cu(II) ions do not interfere in Au(III) binding at pH 3, 4, and 5. All Fe(III) concentrations seem to have no effect on the Au(III) binding at the pH that was investigated. The presence of Ca(II) increases about 50% the binding of Au(III) at pH 6 and decreases about 25% at pH 2, while the presence of Mg(II) ions increased the Au(III) binding to native hop biomass almost 10% at pH 2 and more than 30% at pH 6.

**Key Words:** Gold binding; Binding affinities; Hop biomass; Metal binding; Metal interferences.

## INTRODUCTION

Traditional methods for heavy metal removal from wastewaters such as chemical precipitation, filtration, and electrochemical treatment have some disadvantages. These methodologies utilize expensive equipment, they do not produce a thorough metal removal and they demand continuous monitoring of the systems. Phytofiltration (the use of dead plant tissues) has been used as a technique to remove the toxic metal contamination from wastewaters and natural waters.<sup>[1,2]</sup> Biomasses of algae, bacteria, fungi, and plants have demonstrated different capabilities to accumulate large amounts of heavy metals.<sup>[3,4]</sup> Non-living biomasses mainly consist of proteins, polysaccharides, and lipids including many functional groups such as carboxylate, hydroxyl, sulfhydryl, and amino groups that can bind metal ions.<sup>[5]</sup> The dead tissue of plants appear to have advantages over living plants because they are not only unaffected by high concentrations of the toxic elements but they are also cost-effective. The biosorption of heavy metals by biomasses is affected by several factors such as time, pH, and capacity of the biomass to adsorb specific metals and metal concentrations, among others. The mechanisms of adsorption can occur via ion-exchange, complexation, electrostatic binding, or precipitation.<sup>[6,7]</sup>

Currently, the demand for gold has increased due to its significant applications in technology and industry. This fact has produced the seeking of new technologies for recovering this metal from industrial or mining wastewaters. Typical gold concentration in wastewaters is low but in large volumes and in specific industrial effluents, recovery is convenient, especially if there is an environmentally friendly manner for recovery.<sup>[8,9]</sup> Several biomasses have been studied for their ability to uptake heavy metals and therefore can be used as filters in bioremediation.<sup>[10]</sup> The use of biological systems to recover gold represents an alternative to current technologies such as activated carbon, cyanidation process, and resin ion-exchange.<sup>[11]</sup>

Gardea-Torresdey et al.<sup>[12]</sup> have found that alfalfa biomass has the ability to bind Au(III) ions from solution and reduce them to Au(0) with the



consequent formation of gold nanoparticles. In addition, these researchers showed successful metal sorption from industrial wastewaters using hop biomass.<sup>[13,14]</sup> However, our preliminary results showed that native hop biomass effectively removed Au(III) from solutions containing  $\text{KAuCl}_4$ , reducing Au(III) to Au(0) (unpublished data).

Metals such as Cu and Fe and hard cations such as Ca and Mg are present in wastewater from industrial effluents or sewage.<sup>[15-18]</sup> These cations can affect the adsorption of target metals due to competition for the binding sites in the sorbent agent.<sup>[19]</sup> Therefore, the purpose of this study was to determine the effect of different concentrations of Cu(II), Fe(III), Ca(II), and Mg(II) cations in the binding of Au(III) ions to native hop biomass. Batch experiments were performed using several concentrations of these cations at different pH values while the concentration of Au(III) (using  $\text{KAuCl}_4$ ) solution was kept constant. The results of these studies are reported herein.

## MATERIALS AND METHODS

### Hop Biomass Collection

Hop biomass used for these experiments (from cone belt, harvest portion of the plant) was obtained from plants grown at the USDA-ARS Hop Research Farm located outside Corvallis, Oregon. Plants were allowed to grow to cone maturity before cut down. The cones were separated from the rest of the plant and washed with deionized (DI) water in order to remove dirt and debris. Cone samples were then allowed to air dry for a week, dried in a forced air dryer set at 65°C, and ground with a Wiley-Mill miller. The resulting powder was passed through a 100-mesh sieve to achieve a uniform particle size.

### Batch pH Laboratory Experiments for Cu(II) Interference on Au(III) Binding

This study was performed using a procedure previously published.<sup>[20]</sup> A 500 mg sample of hop biomass was weighed and washed twice with 0.01 M HCl to remove any debris that might interfere with Au(III) binding. Subsequently, the biomass was washed three times with DI water. The washings were collected and dried to account for any biomass lost. The biomass was then centrifuged at 3000 rpm in a Marathon 6K Fisher Scientific Centrifuge for 5 min and resuspended in DI water to a concentration of 5 mg/mL. The pH of the biomass solution was 3.89. Aliquots of this solution were adjusted to pH 2, 3, 4, 5, and 6 by the addition of 1 and 0.1 M NaOH solutions. At each



pH, 4 mL of the biomass solution were transferred to clean 5 mL test tubes and centrifuged for 5 min at 3000 rpm and the supernatants were then discarded. Aliquots of a Au(III) solution (0.1 mM) prepared from  $\text{KAuCl}_4$  were mixed with Cu(II) solutions prepared from  $\text{Cu}(\text{NO}_3)_2$  at concentrations of 0.1, 0.2, 0.3, and 0.4 mM, previously adjusted with sodium hydroxide at pH values of 2, 3, 4, 5, and 6. The biomass was allowed to react separately with a 4 mL of the mixture, the Au(III), and the Cu(II) solutions at each pH and equilibrated for 1 hr, the time previously determined as the optimum for Au(III) binding. After equilibration, the samples were centrifuged and the supernatants transferred to clean test tubes for metal analysis. The metal analyses were performed by ICP-OES. All experiments were performed in triplicate for quality assurance.

### Metal Analysis

A Perkin–Elmer Optima 4300 DV ICP-OES, with a AS-90 plus auto sampler rack was used to determine the elemental concentrations. This instrument is adequate for these analyses because it provides the advantage of low inter-element interference, multi-element detection capability, and low detection limits.<sup>[21]</sup> The gold wavelength with the highest sensitivity was used for analysis (242.7 nm). The operating parameters used for analysis include: nebulizer flow, 0.70 L/min; sample introduction, 1.65 mL/min; flush time, 10 sec; delay time, 60 sec, and wash time, 60 sec. Five standards were prepared from a 1000 ppm stock solution, diluted with DI water and 5% nitric acid was added to avoid pH changes. All correlation coefficients for the calibration curves were 0.999 or higher. Table 1 shows the wavelengths selected for each element as well as their respective correlation coefficients. All samples were measured in triplicate, with the mean value and relative standard deviation recorded.

**Table 1.** Selected wavelengths and correlation coefficients of the calibration curves for the elements analyzed.

Element	Wavelength (nm)	Correlation coefficient
Au	242.795	0.999645
Cu	327.400	0.999980
Fe	259.939	0.999852
Ca	315.887	0.999987
Mg	280.271	0.999757



**Batch Laboratory Experiments for Fe(III) Interference on Au(III) Binding**

These experiments were performed using the method described above in order to determine the interference of Fe(III) on the binding of Au(III) to hop biomass. The native hop biomass was reacted with different solutions of Au(III)–Fe(III), which had Au(III) at 0.1 mM and Fe(III) [from  $\text{Fe}(\text{NO}_3)_3$ ] at concentrations of 0.1, 0.2, 0.3, and 0.4 mM without adjusting the pH because Fe(III) precipitates with the addition of NaOH. The pH of the hop biomass was 3.9 and the pH of the Au–Fe solution ranged from 1.89 to 2.32. The pH decreased when the Fe concentration increased. As mentioned before, the Au(III) concentration remained constant at 0.1 mM in all solutions. A 0.1 mM Au(III) solution reacted with hop biomass was used as a control. The samples were equilibrated for 1 hr, centrifuged, and the supernatants transferred to clean test tubes for metal analyses by ICP-OES and samples were run in triplicate for quality assurance.

**Batch pH Laboratory Experiments for Ca(II) and Mg(II) Interference on Au(III) Binding**

In order to determine the effects of hard water conditions on Au(III) binding, Ca(II) and Mg(II) were added separately in different concentrations to a constant 0.1 mM Au(III) concentration. Each study consisted of increasing concentrations of Ca(II) and Mg(II) in the following order: 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 M. These experiments were carried out under the same conditions as previously described for the batch pH laboratory experiments for Cu(II), at a pH range of 2–6. Again, the Au(III) content was analyzed by ICP-OES and experiments were performed in triplicate. Since Ca(II) and Mg(II) do not bind to hop biomass (unpublished data), the concentrations of these cations in the supernatants were not quantified.

**RESULTS AND DISCUSSIONS****Results for Cu(II) Interference on Au(III) Binding**

Plants contain different compounds such as carboxylate, hydroxyl, sulfate, phosphate, and amino groups that may act as binding sites for

different ions present in wastewater. These varieties of binding sites allow the biomass to bind metal ions at different pH levels.<sup>[22]</sup> Because Cu(II) ions are considered borderline acids (between hard and soft) and Au(III) ions as soft acids according to Pearson's classification,<sup>[23]</sup> Cu(II) ions may either compete for the available binding sites in the biomass or form complexes, which may result in the inhibition or enhancement of the Au(III) binding to hop biomass. Table 2 shows the Au(III) binding after hop biomass was reacted with Au–Cu solutions prepared with different Cu(II) concentrations at different pHs using a constant 0.1 mM concentration of Au(III). A solution 0.1 mM of Au(III) was used as control. As shown in Table 2, at pH values of 3, 4, and 5, the presence of Cu(II) ions did not affect the Au(III) binding to hop biomass. However, at pH 2 there was a decrease of about 10% on Au(III) binding to the biomass when Cu(II) was at concentrations of 0.1, 0.2, and 0.4 mM. When Cu(III) was at 0.3 mM, an increase of 10% on Au(III) binding was observed. According to Gardea-Torresdey et al.,<sup>[24]</sup> the metal binding involves different ligand-exchange mechanisms and electrostatic interactions that play an important role in the adsorption of metal ions to the hop biomass. Even though the binding of two different metals to different binding sites on the biomass changes with the concentration of the metal, the amount of metal bound remains constant.<sup>[25]</sup> As shown in Table 2, from a solution of 0.1 mM Au(III), 82% percent of Au(III) was bound to the hop biomass. Moreover, in Table 2, we see an increase in the binding of Au(III) ions at pH 6 when different concentrations of Cu(II) were added. This is perhaps due to the fact that at pH 6 most of the functional groups including the carboxyl groups are deprotonated, Cu(II) ions are then bound to the carboxyl groups available in the biomass forcing the binding of Au(III) ions to different functional groups. Cu(II) ions decrease the amount of negative charges at higher pHs. Table 3 shows the adsorption of Cu(II) ions to hop biomass. This table shows that at pH 2 the uptake of copper by hop biomass is about 45% at 0.1 mM Cu(II) concentration and this uptake decreases as Cu(II) concentrations increases. This is due to the fact that at pH 2 most of the functional groups involved in the binding of Cu(II) to hop biomass (mostly carboxyl groups) are protonated. In addition, at pH 2, the adsorption of Cu(II) decreased as the concentration increased since the binding sites are being saturated. At pH 3, 4, 5, and 6, the binding of Cu(II) to hop biomass increases due to the availability of carboxyl groups and other functional groups that are deprotonated. These results are comparable to previous results obtained with alfalfa biomass exposed to a multi-metal solution containing Pb(II), Cu(II), Cr(III), Zn(II), Ni(II), and Cd(II).<sup>[26]</sup> These metals did not affect the binding of Au(III) to the alfalfa biomass at any pH. These results suggest that other metal ions were bound

**Table 2.** Percent of Au(III) bound to hop biomass after 1 hr of equilibration with different concentrations of Au(III)–Cu(II) solutions at different pH values.

pH	Solutions	% Au bound	(+/-)
2	Au control	82.17	5.40
	Au 0.1 mM + Cu 0.1 mM	75.36	5.31
	Au 0.1 mM + Cu 0.2 mM	70.88	5.57
	Au 0.1 mM + Cu 0.3 mM	93.44	1.13
	Au 0.1 mM + Cu 0.4 mM	76.07	2.74
3	Au control	98.54	3.28
	Au 0.1 mM + Cu 0.1 mM	100.00	3.53
	Au 0.1 mM + Cu 0.2 mM	100.00	2.30
	Au 0.1 mM + Cu 0.3 mM	99.60	0.69
	Au 0.1 mM + Cu 0.4 mM	99.80	1.06
4	Au control	98.00	1.55
	Au 0.1 mM + Cu 0.1 mM	100.00	2.54
	Au 0.1 mM + Cu 0.2 mM	100.00	2.20
	Au 0.1 mM + Cu 0.3 mM	99.58	1.86
	Au 0.1 mM + Cu 0.4 mM	99.80	0.34
5	Au control	92.31	1.48
	Au 0.1 mM + Cu 0.1 mM	100.00	1.98
	Au 0.1 mM + Cu 0.2 mM	99.76	2.79
	Au 0.1 mM + Cu 0.4 mM	99.19	0.62
	Au 0.1 mM + Cu 0.6 mM	99.52	1.09
6	Au control	53.04	5.07
	Au 0.1 mM + Cu 0.1 mM	96.47	2.78
	Au 0.1 mM + Cu 0.2 mM	91.42	2.80
	Au 0.1 mM + Cu 0.3 mM	89.92	1.24
	Au 0.1 mM + Cu 0.4 mM	96.08	0.50

*Note:* +/– corresponds to a 95% confidence interval.

to the alfalfa biomass at higher pHs due to the availability of carboxyl groups.<sup>[26]</sup> We propose that hop biomass binds both Au(III) and Cu(II) at different binding sites. Cu(II) is considered to be a borderline acid according to the Pearson's classification, in other words, it can be bound to hard or soft bases.<sup>[23]</sup> The ligand groups on biomasses for Cu(II) binding could be carboxylate, thiolate, or phosphates, which are either negatively charged groups or amines that have lone pairs of electrons. Depending on the coordination characteristics of the metal ion, there is a preference for the binding site of the biomass.<sup>[27]</sup> In order to determine these binding sites for Cu(II) in hop biomass, further experiments are needed.



**Table 3.** Percent of Cu(II) bound to hop biomass after 1 hr of equilibration with different concentrations of Cu(II) solutions at different pH values.

pH	Solution	% Cu bound	(+/-)
2	Cu 0.1 mM	44.57	2.34
	Cu 0.2 mM	26.43	3.33
	Cu 0.3 mM	26.01	1.12
	Cu 0.4 mM	20.88	2.54
3	Cu 0.1 mM	58.53	2.03
	Cu 0.2 mM	69.92	2.28
	Cu 0.3 mM	55.87	1.83
	Cu 0.4 mM	42.78	2.35
4	Cu 0.1 mM	83.63	2.73
	Cu 0.2 mM	78.59	2.10
	Cu 0.3 mM	71.31	1.92
	Cu 0.4 mM	63.02	2.26
5	Cu 0.1 mM	88.55	4.60
	Cu 0.2 mM	83.19	1.17
	Cu 0.3 mM	77.98	1.93
	Cu 0.4 mM	71.58	2.05
6	Cu 0.1 mM	92.69	2.92
	Cu 0.2 mM	88.51	1.88
	Cu 0.3 mM	86.20	1.62
	Cu 0.4 mM	80.29	5.77

*Note:* +/- corresponds to a 95% confidence interval.

### Results for Fe(III) Interference on Au(III) Binding

As mentioned before, this study was carried out without pH adjustment of the Fe(III)-hop biomass solution due to the fact that Fe(III) precipitates with the addition of NaOH. The pH of the solutions containing different concentrations of Fe(III) ions was 4.

Table 4 shows the results obtained by exposing hop biomass to different concentrations of Fe(III). These results are similar to those obtained for Cu(II). The concentrations of Fe(III) did not affect the binding of gold to the hop biomass because the uptake of Au(III) by hop biomass in a solution containing 0.1 mM of Au(III) at pH 4 was about 100% (Au control). The percent of Fe(III) bound was quantified also by ICP/OES. However, because Fe(III) is considered a hard acid, it can be bound to hard ligands like carboxyl groups. Studies performed previously have shown that carboxyl groups and other



**Table 4.** Percent of Au(III) bound to hop biomass after 1 hr of equilibration with different concentrations of Au(III)–Fe(III) solutions at pH 4.

pH	Solution	% Au bound	(+/-)	% Fe bound	(+/-)
4	Fe 0.1 mM	100	0.83	45.09	2.02
	Fe 0.2 mM	100	0.41	29.24	1.44
	Fe 0.3 mM	99.80	0.35	25.98	1.11
	Fe 0.4 mM	98.97	0.46	17.63	1.27

Note: +/– corresponds to a 95% confidence interval.

groups present in *Sargassum* biomass participate in the uptake of Fe(III) ions.<sup>[23]</sup> The uptake of Fe(III) ions by *Sargassum* biomass increases at higher pH values rather than at lower pH because at higher pH values more binding groups are deprotonated. Furthermore, Fe(III) ions, which function as hard acids, tend to form strong ionic bonds with carboxylates, which are considered hard bases.<sup>[23]</sup> As it is shown in Table 4, the uptake of Fe(III) ions by hop biomass decreases as the concentration of Fe(III) ions increases. This is probably due to the saturation of the Fe(III) binding sites.

### Results for Ca(II) Interference on Au(III) Binding

This part of the study was conducted to determine the influence of Ca(II) on the binding of Au(III) to hop biomass. We conducted these experiments using Au(III) at 0.1 mM and Ca(II) at various concentrations at a pH range of 2–6.

Table 5 shows the data collected for the Ca(II) interference study. The binding of Au(III) to hop biomass at pH 2 decreased by about 10%, and at pH 3 about 5% in comparison to experiments without the addition of Ca(II) ions (Au control). As observed in Table 5, the Au(III) bound to hop biomass at pH 4 and pH 5 remained nearly constant at all Ca(II) concentrations. At pH 6, an increase of about 45% in Au(III) binding is observed in comparison with the Au(III) control. This may be due to a synergistic effect of Ca(II) ions on Au(III) binding. Ca(II) ions are considered hard acids, which form strong ionic bonds with hard bases and do not compete for the binding sites preferred by Au(III) ions such as sulphydryl and amino groups.

### Results for Mg(II) Interference on Au(III) Binding

Table 6 shows the data collected for Mg(II) interference on Au(III) binding to hop biomass. At pH values of 2–5, the results are similar to those



**Table 5.** Percent of Au(III) bound to hop biomass after 1 hr of equilibration with different concentrations of Au(III)-Ca(II) solutions at different pH values.

pH	Solutions	% Au bound	(+/-)
2	Au control	82.17	5.40
	Au 0.1 mM + Ca 0.1 mM	63.56	4.13
	Au 0.1 mM + Ca 0.2 mM	62.82	2.88
	Au 0.1 mM + Ca 0.4 mM	58.59	3.28
	Au 0.1 mM + Ca 0.6 mM	58.78	4.67
	Au 0.1 mM + Ca 0.8 mM	56.73	2.81
	Au 0.1 mM + Ca 1.0 mM	62.30	2.88
3	Au control	98.54	3.28
	Au 0.1 mM + Ca 0.1 mM	90.03	5.72
	Au 0.1 mM + Ca 0.2 mM	89.98	6.00
	Au 0.1 mM + Ca 0.4 mM	90.39	1.11
	Au 0.1 mM + Ca 0.6 mM	83.11	3.60
	Au 0.1 mM + Ca 0.8 mM	79.50	5.84
	Au 0.1 mM + Ca 1.0 mM	82.42	2.52
4	Au control	98.00	1.55
	Au 0.1 mM + Ca 0.1 mM	96.53	2.38
	Au 0.1 mM + Ca 0.2 mM	95.98	2.46
	Au 0.1 mM + Ca 0.4 mM	95.47	1.62
	Au 0.1 mM + Ca 0.6 mM	96.59	3.69
	Au 0.1 mM + Ca 0.8 mM	95.32	2.94
	Au 0.1 mM + Ca 1.0 mM	95.13	3.53
5	Au control	92.31	1.48
	Au 0.1 mM + Ca 0.1 mM	89.84	1.65
	Au 0.1 mM + Ca 0.2 mM	92.21	1.29
	Au 0.1 mM + Ca 0.4 mM	91.45	2.31
	Au 0.1 mM + Ca 0.6 mM	92.80	2.57
	Au 0.1 mM + Ca 0.8 mM	90.62	1.93
	Au 0.1 mM + Ca 1.0 mM	92.69	4.28
6	Au control	53.04	5.07
	Au 0.1 mM + Ca 0.1 mM	85.34	3.66
	Au 0.1 mM + Ca 0.2 mM	90.28	3.72
	Au 0.1 mM + Ca 0.4 mM	88.42	3.42
	Au 0.1 mM + Ca 0.6 mM	87.30	3.90
	Au 0.1 mM + Ca 0.8 mM	87.91	1.69
	Au 0.1 mM + Ca 1.0 mM	91.43	2.81

*Note:* +/− corresponds to a 95% confidence interval.



**Table 6.** Percent of Au(III) bound to hop biomass after 1 hr of equilibration with different concentrations of Au(III)-Mg(II) solutions at different pH values.

pH	Solutions	% Au bound	(+/-)
2	Au control	82.17	5.4
	Au 0.1 mM + Mg 0.1 mM	90.94	3.44
	Au 0.1 mM + Mg 0.2 mM	93.91	0.14
	Au 0.1 mM + Mg 0.4 mM	93.81	0.13
	Au 0.1 mM + Mg 0.6 mM	93.75	0.08
	Au 0.1 mM + Mg 0.8 mM	91.60	0.08
	Au 0.1 mM + Mg 1.0 mM	92.87	0.68
3	Au control	98.54	3.28
	Au 0.1 mM + Mg 0.1 mM	94.33	0.24
	Au 0.1 mM + Mg 0.2 mM	94.30	0.11
	Au 0.1 mM + Mg 0.4 mM	94.19	0.09
	Au 0.1 mM + Mg 0.6 mM	94.17	0.09
	Au 0.1 mM + Mg 0.8 mM	94.38	0.10
	Au 0.1 mM + Mg 1.0 mM	94.16	0.09
4	Au control	98.00	1.55
	Au 0.1 mM + Mg 0.1 mM	89.53	4.66
	Au 0.1 mM + Mg 0.2 mM	89.69	0.20
	Au 0.1 mM + Mg 0.4 mM	86.35	0.16
	Au 0.1 mM + Mg 0.6 mM	90.29	0.04
	Au 0.1 mM + Mg 0.8 mM	90.62	0.10
	Au 0.1 mM + Mg 1.0 mM	90.11	0.13
5	Au control	92.31	1.48
	Au 0.1 mM + Mg 0.1 mM	88.86	0.32
	Au 0.1 mM + Mg 0.2 mM	90.11	0.13
	Au 0.1 mM + Mg 0.4 mM	87.52	0.34
	Au 0.1 mM + Mg 0.6 mM	87.13	0.06
	Au 0.1 mM + Mg 0.8 mM	88.34	0.16
	Au 0.1 mM + Mg 1.0 mM	89.44	0.08
6	Au control	53.04	5.07
	Au 0.1 mM + Mg 0.1 mM	84.71	0.36
	Au 0.1 mM + Mg 0.2 mM	84.84	0.36
	Au 0.1 mM + Mg 0.4 mM	83.96	0.20
	Au 0.1 mM + Mg 0.6 mM	84.82	0.17
	Au 0.1 mM + Mg 0.8 mM	84.43	0.11
	Au 0.1 mM + Mg 1.0 mM	88.32	0.10

*Note:* +/− corresponds to a 95% confidence interval.



obtained for Ca(II). The binding of Au(III) to hop biomass at this pH range increased about 5–10% and at pH 6 the binding of Au(III) to hop biomass increased about 45%.

Previous batch experiments have shown that higher concentrations of Ca(II) and Mg(II) ions affect the binding of metals like cadmium, chromium, copper, nickel, lead, and zinc to alfalfa biomass, in which the reduction on metal binding was approximately of 40% with exposure to 1 M concentration of Ca(II) and Mg(II) ions.<sup>[28,29]</sup>

Since Mg(II) ions are considered either hard or borderline hard–soft acids, they do not have binding affinity to the functional groups on hop biomass. The specificity of the Au(III) to certain binding sites is determined by stability constants, and hop biomass demonstrated selectivity binding to Au(III) ions. The binding constants of ligands involved in this selective binding could be responsible for the Au(III) binding to hop biomass. In addition, functional groups inside hop biomass such as amino and sulfhydryl groups have a higher stability constant when bound to heavy metals than for calcium and magnesium cations.<sup>[29]</sup> More experimentation is needed to explain these different binding mechanisms.

## CONCLUSIONS

Our results show that hop biomass has the ability to bind Au(III) ions from aqueous solutions without interference of Fe(III) ions at different concentrations. Using different concentrations of Cu(II), an increase on the binding of Au(III) ions to hop biomass was observed at pH 6. The binding of Cu(II) and Fe(III) ions to hop biomass may be accomplished by a different mechanism that does not compete for the gold binding site. In addition, binding trends similar to Cu(II) were found with the addition of Ca(II) and Mg(II) ions, which are commonly present in wastewaters. The results indicate that these ions do not affect the binding of Au(III) to hop biomass at pHs lower than 5. Further studies are being performed in order to determine the functional groups involved in the binding of Au(III) to hop biomass.

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