

Metallic Affinity of Toxic and Noble Metals by Particles Produced from Sericin, Alginate and Poly-(Ethylene Glycol)

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Biosorbents have been used as a potential alternative to the conventional technologies for removal of toxic metals from water and wastewater. The use of waste material as adsorbent offers significant advantages like low-cost, availability, efficiency, biodegradability, etc. In this study, particles produced from a blend between sericin, alginate and Poly(ethylene glycol) diglycidyl ether (PEG) were used to remove toxic and precious metals from aqueous solutions. Precious metals are found in wastewaters of various industrial processes including metal, ore processing, electronic manufacturing and mining; and the recovery of these metals is profitable to those industrial processes. Sericin is a protein present in cocoon of silkworm (*Bombyx mori*) usually discharged in the effluent of silk production. Alginate is a natural polysaccharide extracted from abundant sources of brown algae (brown seaweed) properties to this material. The addition of PEG into a blend of sericin-alginate induces chemical modification that can develop better properties to this material. The objective of this work is to evaluate the metallic affinity and adsorption capacity of particles produced by sericin-alginate blend and sericin-alginate-PEG blend. The blends were dripped in aqueous and alcoholic (ethanol) solutions of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$, and then the particles were dried at 100 °C. The simulation of speciation diagrams as functions of pH was performed using Hydra/Medusa software in order to establish the pH to be used in the experiments. The removal of chromium, cadmium, nickel, copper, lead, silver, palladium, platinum and gold ions from aqueous solution by sericin-alginate particles was evaluated through adsorption affinity testes. The results indicated that the presence of PEG improve the adsorption capacity of the biosorbents. For the noble metals the greatest values of reduction and adsorption capacity were obtained to gold (98 – 99 %) and palladium (87 – 89 %), and for the toxic metals it was obtained higher values of reductions to lead (66 – 83 %), cadmium (62 – 79 %), chromium (69 – 74 %) and copper (65 – 74 %).

1. Introduction

Recently, many researches have focused on using alternative materials in the adsorption process. The high costs of conventional current industrial adsorbents and the abundance of low-cost raw materials from agriculture and industrial waste, biomass, among others, encourages the search for new materials that are able to amalgamate low-cost and satisfactory efficiency of sorption. In this context, sericin and alginate is an interesting alternative due its interaction with a variety of cations (Gimenes et al., 2014), including ionic metals (Silva et al., 2016), drugs (Silva et al., 2015), dyes (Xinqing et al., 2012), and other contaminants.

Sericin is a globular and water soluble protein (Zhang, 2002) whose molecular weight range from 24 kDa (Takasu et al., 2002) to values higher than 400 kDa (Silva et al., 2014a). This macromolecular protein is deposited in layers on the silk fiber (fibroin), by the silk larvae, gluing the threads and allowing the formation of the cocoon (Zhang, 2002). The presence of polar side chain made of hydroxyl, carboxyl and amino groups in this protein enable easy cross-linking, copolymerisation and blending with other polymers to produce biodegradable products with better properties (Dash et al., 2009). In the manufacturing of silk, the sericin is

removed from the silk fibers (fibroin) and discharged as a waste of the process (Zhang, 2002) leading to environmental contamination due its high organic matter content (Aranwit et al., 2012).

Alginate is a natural exopolymer composed of β -1,4 linked D mannuronic and L-guluronic acids. It is extracted from some kind of bacteria (*Pseudomonas spp.* and *Azotobacter spp.*) and from mainly brown seaweed (Nayak and Lahiri, 2005). The polysaccharide alginate is biodegradable, cheap and easy available, because its natural abundant sources (Silva et al., 2016). Alginic acid and its carboxylic salts are biopolymers, which show interesting features such as biocompatibility, biodegradability, viscosifying and the ability of gelation with multivalent cation (Daemi and Barikani, 2012). Divalent cations, like Ca^{2+} , cooperatively bind between adjacent alginate chains, producing the so-called "egg-box" structure, creating ionic interchain bridges, which cause gelling of aqueous alginate solutions (Finotelli et al., 2008).

The objective of the present work is evaluating the metallic affinity of toxic and precious by particles produced from sericin, alginate blend. The presence of the poly(ethylene glycol), as crosslinking agent, in the blend was also investigate. The blends were dripped in aqueous and alcoholic (ethanol) solutions of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$, and then the particles were dried at 100 °C. The metallic affinity for toxic metals: copper (Cu^{2+}), nickel (Ni^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}), lead (Pb^{2+}), chromium (Cr^{3+}) and noble metals: palladium (Pd^{2+}), platinum (Pt^{4+}), gold (Au^{+3}), silver (Ag^+) were investigated in this work.

2. Materials and methods

The *Bombyx mori* silkworm's cocoons were provided by Bratac Company – Londrina/PR – Brazil. All reagents used in this work were analytical grade.

2.1 Preparation of cocoons, sericin extraction and particles production

The first step of materials preparation was the cleaning of *Bombyx mori* cocoons. All dirties in cocoons were cut off and then the material was sliced in small pieces (about 1 cm^2). The cocoons were washed in tap water and rinsed abundantly in deionised water. After the material cleaning, it was dried at 40 °C until constant weight at this temperature. The degumming process in autoclave at 120 °C (1 kgf/cm^2 for 40 min) was performed to remove the sericin from the cocoons. The ratio of cocoons and ultrapure water was 40 : 1,000 (g of cocoons: mL of ultrapure water). The sericin solution (SS), still hot, was filtered to remove the fibers of fibroin and stored in a sealed bottle at room temperature for 12 h (Silva et al, 2014b). After this period, the SS solution was frozen for, at least, 24 h in a conventional refrigerator (- 4 °C) and then it was thawed at room temperature (Silva et al., 2014a). The freezing procedure promotes the precipitation of high molecular weight sericin, which can be recovered by filtration. The filtered sericin was heated in autoclave (120 °C for 10 min) to solubilise again the protein and then the concentration was adjusted by dilution to 25 g/L (Silva et al., 2016).

The sodium alginate (Sigma Aldrich brand) was added in adjusted SS solution in a concentration of 20 g/L. The blend was mixed at 5,000 rpm (Ultraturrax ® T18 - USA) until it was homogeneous. In the particles where PEG (Poly(ethylene glycol) diglycidyl ether - average Mn 526 – Sigma Aldrich) were present, the crosslinking agent was added in the blend in a concentration of 5 g/L, and it was mechanically agitated for 30 min. The particles were prepared by ionic gelation technique where the blend was dripped with a peristaltic pump in alcoholic (ethanol) or aqueous solutions of CaCl_2 (3 % m/V) or $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (6.4 % m/V) (same concentration of Ca^{2+} in both solutions). The Ca^{2+} present in these solutions is responsible for the crosslinking of alginate, present into the blend, and formation of particles. The particles were agitated in Jar-test for 24 h and then it was washed in tap water, to remove the excess of Ca^{2+} , and rinsed, abundantly, with deionised water. The produced particles were dried at a continuous flow oven at 40 °C, and then it was thermal crosslinked at 100 °C for 24 h (Silva et al., 2016). Table 1 presents the blend formulation and the fabrication method of the produced particles.

Table 1: Formulations and methods of preparation of the produced particles

Particle	Blend formulation (g/L) [Sericin / Alginate / PEG]	Calcium Solution (solution in which the particles were produced)
1	25 g/L / 20 g/L / 0 g/L	Aqueous solution of CaCl_2
2	25 g/L / 20 g/L / 0 g/L	Alcoholic solution of CaCl_2
3	25 g/L / 20 g/L / 0 g/L	Aqueous solution of $\text{Ca}(\text{NO}_3)_2$
4	25 g/L / 20 g/L / 0 g/L	Alcoholic solution of $\text{Ca}(\text{NO}_3)_2$
5	25 g/L / 20 g/L / 5 g/L	Aqueous solution of CaCl_2
6	25 g/L / 20 g/L / 5 g/L	Alcoholic solution of CaCl_2
7	25 g/L / 20 g/L / 5 g/L	Aqueous solution of $\text{Ca}(\text{NO}_3)_2$
8	25 g/L / 20 g/L / 5 g/L	Alcoholic solution of $\text{Ca}(\text{NO}_3)_2$

2.2 Metal speciation study and Metal Affinity tests of single components

Chemical Equilibrium Diagrams were simulated using the Hydra/Medusa Software (Puigdomenech, 2010). The metal speciation diagrams is useful to identify the different species of metals and its compounds, as a function of pH. From these diagrams, it is possible to define the pH range in which there are soluble ionic species and the pH value from which occurs the precipitation of metal species. In experiments, it is important to choose the pH value in which only the adsorption process is responsible for decreasing of metal concentration during experiments. For noble metals, a review in literature was conducted to choose the pH of these experiments.

Metal solutions of 1 mmol/L of toxic metals: copper (Cu^{2+}), nickel (Ni^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}), lead (Pb^{2+}), chromium (Cr^{3+}) – and noble metals: palladium (Pd^{2+}), platinum, gold, silver (Ag^+). The solutions were prepared dissolving the salts: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Pb}(\text{NO}_3)_2$; $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; PdCl_2 ; $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$; $\text{H}(\text{AuCl}_4) \cdot 3\text{H}_2\text{O}$, AgNO_3 in ultrapure water (Mili-Q Millipore System). For the affinity tests, 0.5 g of each particle was immersed in 50 mL of each metal solution using Erlenmeyers flasks of 125 mL. The recipes were maintained under agitation (200 rpm) for 24 h at 25 °C (Incubated Saker, SI 600R, Lab Companion Jeio Tech, Korea). It is safe to consider that after this period the adsorption process has reached the equilibrium. Solution of diluted nitric acid (5 %) was used to adjust the pH of the metallic solutions before and during the experiments. After 24 h of agitation, the particles were removed and samples solutions were centrifuged at 4,000 rpm for 10 min. The metal concentrations were measured at atomic absorption spectroscopy (AAS – 7000A – Shimadzu) according to equipment instructions.

The adsorption capacity (q_e) of each particle at equilibrium state and the percentage removal (%R), in the evaluated conditions, were determined by Eqs(1) and (2), respectively.

$$q_e = \frac{(C_0 - C_e) \cdot V}{m_p} \quad (1)$$

where, C_0 is the initial concentration of solutions (1 mmol/L), C_e is the equilibrium concentration after 24 h of adsorption in batch process, V is the volume of metal solution (50 mL), and m_p is the dry mass of the particles (0.5 g).

$$\%R = \frac{(C_0 - C_e)}{C_0} \cdot 100 \% \quad (2)$$

3. Results and discussion

The speciation diagrams as function of pH, to toxic metal were performed by Hydra/Medusa Software. In Figure 1, these diagrams are presented.

From Figure 1, it can be seen that soluble ionic fraction of the toxic metals occurs in pH less than 5.2 to copper, 6.7 to nickel, 8.2 to cadmium, 5.2 to zinc, 5.4 to lead and 3.6 to chromium. The speciation diagram of zinc indicates that from pH 5.2 there is formation of the chemical ionic specie $\text{Zn}(\text{OH})^+$ and from 7.1 the precipitated specie $\text{ZnO}_{(\text{cr})}$ starts to be formed in solution. The chromium diagram shows that from pH 3.6 there is a formation of precipitated $\text{Cr}_2\text{O}_3_{(\text{cr})}$, but in pH less than 3.6 there are also another ionic species in solution, besides the single specie Cr^{3+} . In order to evaluate the adsorption of these metals in affinity tests, the pH was adjusted and controlled during the experiments to values between 3.0 - 3.5. All the experiments were performed at the same pH in order to allow the comparison of obtained results. In this range of pH only the soluble chemical compounds ionic are present. This procedure was conducted to avoid the chemical precipitation during the experiments. This way, there is safety in affirming that the cause of reduction of metal concentration, observed posteriorly, is exclusively due the adsorption process.

For noble metal, the Hydra database is not accurate for making speciation diagrams. There are not all ionic species of the salts of these precious metals. An approach using the ionic species available in the Hydra database was performed and the diagrams indicate that in pH close to zero there is already the formation of precipitated species. So, a review in the literature was done to investigate what range of pH can be used to perform the metallic affinity tests of noble metal. For the metallic affinity experiments of noble metals, the pH was adjusted to values between 2.5 (Chen et al., 2011) and 3.0 (Lam et al., 2006).

The percentage removal (%R) and the adsorption capacity (q_e) of each particle for each metal at equilibrium state are presented in Table 2 and Table 3, respectively.

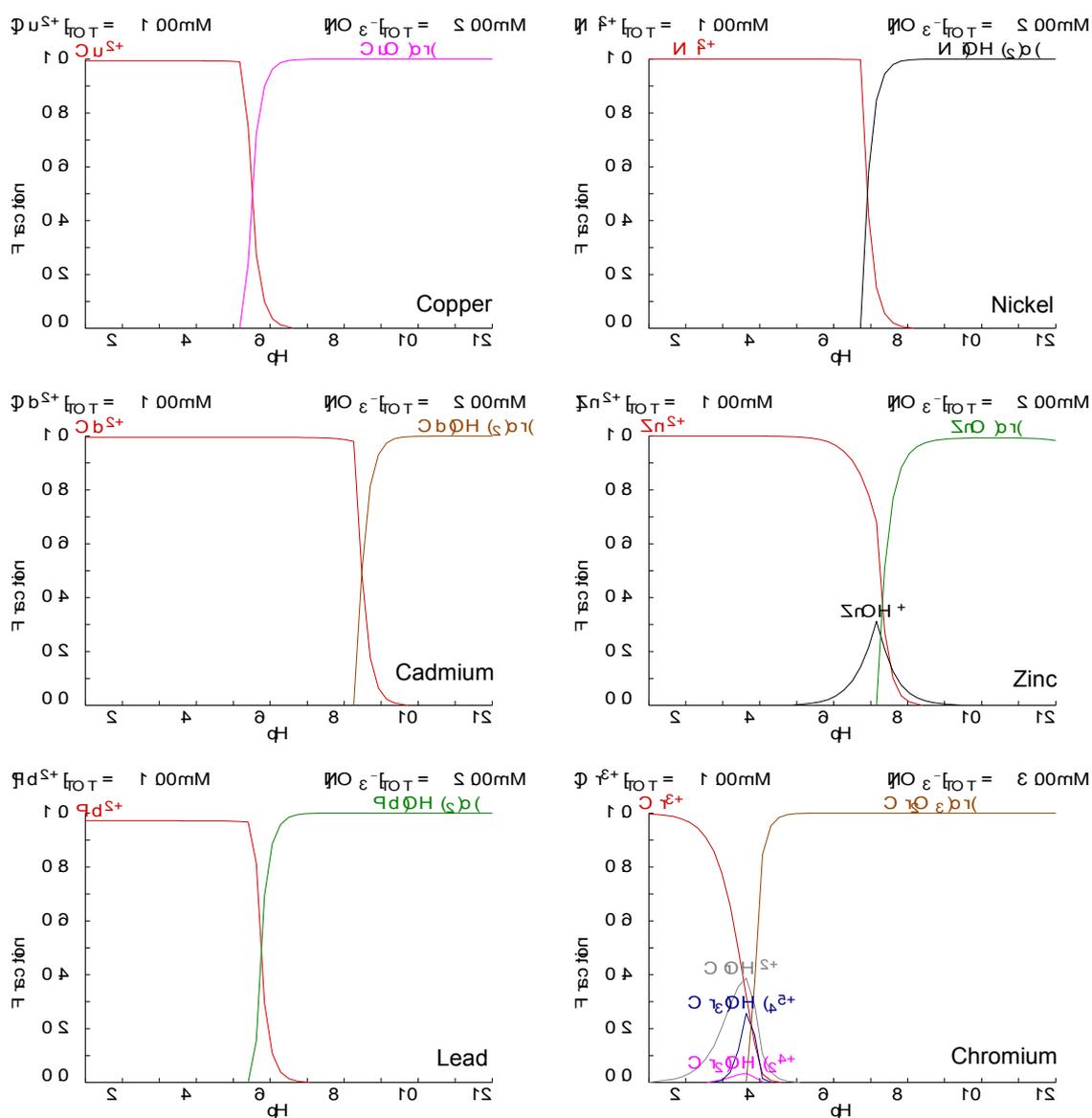


Figure 1: Metal speciation diagrams of copper (Cu^{2+}), nickel (Ni^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}), lead (Pb^{2+}), chromium (Cr^{3+}) as function as pH.

Table 2: Percentage removal (%R - %) of the metal concentration in solution by sericin/alginate/PEG particles

Metal:	Pd	Pt	Au	Ag	Cu	Cd	Ni	Pb	Zn	Cr
Part. 1	87.13	73.11	98.86	-	65.04	62.23	14.75	65.89	15.62	73.16
Part. 2	88.65	71.77	99.15	-	73.85	70.71	15.48	81.99	21.92	70.97
Part. 3	88.63	66.35	99.38	61.31	74.38	72.11	23.46	79.95	24.05	74.41
Part. 4	88.87	70.30	99.24	60.42	71.40	73.62	13.98	83.21	28.45	71.99
Part. 5	86.78	74.41	99.28	-	74.85	70.70	19.72	82.32	17.70	73.32
Part. 6	86.88	73.67	99.70	-	72.85	70.90	12.01	81.77	22.32	71.75
Part. 7	88.92	71.59	99.70	63.36	73.09	79.63	23.71	82.76	27.84	73.67
Part. 8	89.00	73.22	99.66	60.98	74.23	79.61	13.33	83.32	30.23	69.64

After 24 h there is an equilibrium state in the system, or, the adsorption process is not anymore able to reduce the metal concentration in solution. Because the silver (Ag^+) precipitates in presence of chlorine, the affinity experiments of particles 1, 2, 5 and 6 (experiments with particles produced in $CaCl_2$ solution) were not executed and results will not be shown.

Table 3. Adsorption capacity (q_e – mmol of metal/g of particle) of the sericin/alginate and sericin/alginate/PEG particles for each metal.

Metal:	Pd	Pt	Au	Ag	Cu	Cd	Ni	Pb	Zn	Cr
Part. 1	0.087	0.073	0.099	-	0.065	0.062	0.015	0.066	0.016	0.073
Part. 2	0.089	0.072	0.099	-	0.074	0.071	0.015	0.082	0.022	0.071
Part. 3	0.089	0.066	0.099	0.061	0.074	0.072	0.023	0.080	0.024	0.074
Part. 4	0.089	0.070	0.099	0.060	0.071	0.074	0.014	0.083	0.028	0.072
Part. 5	0.087	0.074	0.099	-	0.075	0.071	0.020	0.082	0.018	0.073
Part. 6	0.087	0.074	0.100	-	0.073	0.071	0.012	0.082	0.022	0.072
Part. 7	0.089	0.072	0.100	0.063	0.073	0.080	0.024	0.083	0.028	0.074
Part. 8	0.089	0.073	0.100	0.061	0.074	0.080	0.013	0.083	0.030	0.070

From Table 2 and Table 3, it can be seen that the adsorption process of toxic metal: Cu, Cd, Pb and Cr, present high percentage reduction and q_e values, with the highest values to lead. Considering that in the experimental conditions the maximum q_e value that could be reached is 0.1 mmol/g, the obtained results to copper, cadmium, lead and chromium are satisfactory. To nickel and zinc adsorption, the obtained results indicate the sericin/alginate and sericin/alginate/PEG particles are not feasible because of the low reduction and q_e values. With exception to silver, which results were slightly lower those for Cu, Cd, Pb, and Cr metal ions, the results observed to noble metals (Pd, Pt and Au) showed greater values than the ones observed to toxic metals. The similarity observed in the reduction and q_e values for Pd, Pt and Au, indicate that, to these metals, the different formulations and preparation methods do not promote changes in the particles that could improve the capacity adsorption in a significant way. Probably this fact is due the high value observed, near the maximum possible value, meanly to palladium and gold.

According to Gimenes et al. (2007) the presence of ethanol in sericin production materials increase the aggregated strands (β -sheet), whereas both random coil and α -helix components decrease in the secondary structure of the sericin. The results observed by the particles produced in ethanol solution (particles 2, 4, 6 and 8), in general, do not show significant difference then the ones produced in aqueous solution. It seems that the changes in the secondary structure do not promote improvements in the capacity of the adsorbent for these metals.

According to Cho et al. (2003), PEG possesses as amphipathic behaviour, and the introduction of this cross-linking agent of protein develop modifications in its structure. In general, the particles in which PEG is present in formulation, present a slightly higher range of %R and q_e . For example, for %R to copper the range observed was [65.04 – 73.85 %] for the particles without PEG and [72.85 – 74.85 %] for the particles with PEG. For Cd the range observed was [62.23 – 73.62 %] to the particles without PEG and [72.85 – 74.85 %] to the particles with PEG. Similar behaviour was observed to nickel, lead and zinc. Thus, the modifications, promoted by PEG in the structure of the particles, seem to improve the adsorption capacity of the adsorbent.

4. Conclusions

In order to compare the results, the speciation study of the metal ions was performed and the maximum value of pH allowed in the experiments were 3.5 and 3.0 to toxic and noble metals. The blend between sericin/alginate and sericin/alginate/PEG present a complex composition, due their chemical characteristics, and the results of metallic affinity tests showed that, in general, the produced particles could achieve high values of reduction percentage and adsorption capacity. To noble metals, the greatest results were obtained to Au, Pd and Pt, and to toxic metals Pb, Cd, Cr and Cu. The results also showed that the particles are no feasible to adsorption of Ni, due the low percentage removal observed. The alcohol in the production processes of the particles seems does not improve the capacity of these adsorbents, but the PEG in their compositions promotes changes that slightly improved the obtained results in metallic affinity tests.

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