Hexavalent Chromium Removal by *Litchi chinensis* Sonn Peel

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**Abstract:** Problem statement: We studied the Chromium (VI) removal capacity in aqueous solution by the litchi peel. **Approach:** We use the diphenylcarbazide method to evaluate the metal concentration. **Results:** The highest biosorption of the metal (50 mg L\(^{-1}\)) occurs within 6 min, at pH of 1 and 28°C. According to temperature, the highest removal was observed at 40 and 50°C, in 45 min, when the metal (1 g L\(^{-1}\)) was completely adsorbed. At the analyzed concentrations of Cr (VI), litchi peel, showed excellent removal capacity, besides it removes efficiently the metal *in situ* (100% removal, 5 days of incubation, 5 and 10 g of biomass). After 1 h of incubation the studied biomass reduces 1.0 g of Cr (VI) with the simultaneous production of Cr (III). **Conclusion:** The shell can be used to eliminate it from industrial wastewater.

**Key words:** Cr (VI), removal, litchi peel, bioremediation, diphenylcarbazide

**INTRODUCTION**

Chromium (Cr) toxicity is one of the major causes of environmental pollution emanating from tannery effluents. This metal is used in the tanning of hides and leather, the manufacture of stainless steel, electroplating, textile dyeing and as a biocide in the cooling waters of nuclear power plants, resulting chromium discharges causing environmental concerns (Bai and Abraham, 2001). Cr exists in nine valence states ranging from -2+6. From these, only the hexavalent [Cr (VI)] and trivalent chromium [Cr (III)] have primary environmental significance due they are the most stable oxidated forms in the environment. Both are found in various bodies of water and wastewaters (Seng and Wang, 1994). Cr (VI) typically exists in one of these two forms: chromate (CrO\(_4^{2-}\)) or dichromate (Cr\(_2\)O\(_7^{2-}\)), depending on the pH of the solution (Seng and Wang, 1994). These two divalent oxyanions are very water soluble and poorly adsorbed by soil and organic matter, making them mobile in soil and groundwater. Both chromate anions represent acute and chronic risks to animals and human health, since they are extremely toxic, mutagenic, carcinogenic and teratogenic (Marsh and McInerney, 2001). In contrast to Cr (VI) forms, the Cr (III) species: predominantly hydroxides, oxides or sulphates, are less water soluble, mobile (100 times less toxic) (Nriagu and Nieboer, 1988) and (1,000 times less) mutagenic (Lofroth and Ames, 1978). The principal techniques for recovering or removing Cr (VI), from wastewater are: chemical reduction and precipitation, adsorption on activated carbon, ion exchange and reverse osmosis. In a basic medium (Park *et al*., 2004a). However, these methods have certain drawbacks, namely high cost, low efficiency, generation of toxic sludge or other wastes that require disposal and imply operational complexity (Sahin and Ozturk, 2005).

In this context, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous effluents (Volesky and Holan, 1995). The process of heavy metal...
removal by biological materials is known as biosorption. Biomass viability does not affect the metal uptake. Therefore any active metabolic uptake process is currently considered to be a negligible part of biosorption. Various biosorbents have been tried, which include seaweeds, moulds, yeast, bacteria, crab shells, agricultural products such modified corn stalks, (Chen et al., 2011), hazelnut shell (Cimino et al., 2000), orange waste (Perez-Marin et al., 2007) and tamarind peel (Acosta et al., 2010). It has also been reported that some of these biomass can reduce chromium (VI) to chromium (III), like tamarind peel (Acosta et al., 2010), tea fungal biomass (Razmovski and Sciban, 2007); Mesquite (Aldrich et al., 2003), Eucalyptus bark (Sarin and Pant, 2006), red roses waste biomass (Shafqat et al., 2008) and Yohimbe bark (Fiol et al., 2008). The present study is undertaken with following objective: Investigate the use of Litchi chinensis Sonn peel for the biosorption of Chromium (VI) in aqueous solution.

MATERIALS AND METHODS

Biosorbent used:
Litchi chinensis sonn peel: Litchi peel was obtained from the fruits harvested between the months of June-September 2010, in the towns of Matlapa and Axtla de Terrazas, San Luis Potosi, SLP, Mexico. To obtain the biomass, litchi rind washed with water trideionized 72 h under constant stirring, with water changes every 12 h. Subsequently, boiled 1 h to remove traces of the fruit was dried at 80°C. For 12 h in the oven, ground in blender and stored in amber vials until use.

Determination of hexavalent, trivalent and total Cr:
Hexavalent Cr and trivalent chromium were quantified by a spectrophotometric method employing diphenylcarbazide and chromazurol S, respectively (Clesceri et al., 1998; Pantaler and Pulyaeva, 1985), total Cr was determined by electrothermal atomic absorption spectroscopy (Clesceri et al., 1998).

The values shown in the results section are the mean from three experiments carried out by triplicate.

RESULTS AND DISCUSSION

Effect of incubation time and pH: Fig. 1 shows the effect of the incubation time and pH. The optimum time and pH for Cr (VI) removal was 5 min and pH 1.0, at constant values of biosorbent dosage (1 g 100 mL⁻¹), initial metal concentration (50 mg L⁻¹) and temperature (30°C).
**Effect of initial metal concentration:** On the other hand, at low metal concentrations (100 and 200 mg L\(^{-1}\)), biomass studied, shows the best results for removal, adsorbing 100% at 10 and 20 min respectively, while 1000 mg L\(^{-1}\) of metal is removed 100% up to 195 min of incubation at 28°C (Fig. 3). Also, we observed the development of a blue-green and a white precipitate, which changes more rapidly at higher temperatures (date not shown). The results are coincident for tamarind peel and seeds (Acosta *et al.*, 2010; Agarwal *et al.*, 2006). The increase in initial concentration of Cr (VI) results in the increased uptake capacity and decreased the percentage of Cr (VI) removal. This was due to the increase in the number of ions competing for the available functional groups on the surface of biomass (Agarwal *et al.*, 2006).

**Cr (VI) Removal by different biomasses:** We studied the Cr (VI) (100 mg L\(^{-1}\)) removal, with 1 g of different biomass. Litchi peel was the most efficient, because in 10 min at 28°C remove 100% of the metal, followed by xylan and polygalacturonic acid (150 and 300 min at 60°C, respectively) and starch and cellulose were less efficient (43.6% at 28°C and 300 min of incubation and 21.83% at 60°C at the same time of incubation, respectively) (Fig. 4). With respect to other biomass used, most authors report lower removal efficiencies of metal, for example: 45 mg L\(^{-1}\) for eucalyptus bark (Sarin and Pant, 2006), 13.4 and 17.2 mg L\(^{-1}\) for bagassa and sugar cane pulp, 29 mg L\(^{-1}\) coconut fibers, 8.66 mg L\(^{-1}\) for wool (Dakiki *et al.*, 2002), 25 and 250 mg L\(^{-1}\) of chitin and chitosan (Sag and Aktay, 2002) and 1 mg L\(^{-1}\) for cellulose acetate (Arthanareeswaran *et al.*, 2007).

**Cr (VI) Removal in the presence of different heavy metals:** We analyzed whether the presence of different metals interfere with the Cr (VI) removal (500 mg L\(^{-1}\)) at a pH of 1.0, with 1 g of litchi peel, finding that none of the added metals (cadmium, copper, zinc and mercury) interferes with the Cr (VI) removal, but in the presence of zinc and mercury takes 10-20 min longer to remove 100% of the metal (Fig. 5). This is consistent with many reports in the literature (Bai and Abraham, 2001; Acosta *et al.*, 2010; Sarin and Pant, 2006; Leyva-Ramos *et al.*, 2005; Shaukat, 2011).

**Time course of Cr (VI) decrease and Cr (III) production:** The ability of the *Litchi chinensis* Sonn peel to lower the initial Cr (VI) of 1.0 g L\(^{-1}\) and Cr (III) production in solution was analyzed. Figure 6 shows that the shell exhibited a remarkable efficiency to diminish Cr (VI) level with the concomitant production of Cr (III) in the solution (indicated by the formation of a blue-green color and a white precipitate and his determination for Cromazurol S, date not shown) (Pantaler and Pulyaeva, 1985).
Fig 5: Effect of different metals concentration on Chromium (VI) removal. By *Litchi chinensis* Sonn peel. 500 mg L\(^{-1}\) of metal. 1.0 g of litchi biomass pH 1.0. 100 rpm. 28°C

Thus, after 1 h of incubation, the shell biomass caused a drop in Cr (VI) from its initial concentration of 1.0 g L\(^{-1}\) to almost undetectable levels and the decrease level occurred without change significant in total Cr content. As expected, total Cr concentration remained constant over time, in solution control. These observations indicate that litchi peel is able to reduce Cr (VI) to Cr (III) in solution. Furthermore, as the *Litchi chinensis* Sonn peel contains vitamin C and some carbohydrates, we found that vitamin C and cystine quickly reduce Cr (VI) to Cr (III) and could be very important part in the metal reduction, confirming some reports in the literature (Seng and Wang, 1994; Acosta et al., 2012; Xu et al., 2005; Yong et al., 2005). There are two mechanisms by which chromate could be reduced to a lower toxic oxidation state by an enzymatic reaction. Currently, we do not know whether the shell biomass used in this study express and Cr (VI) reducing enzyme(s). Further studies are necessary to extend our understanding of the effects of coexisting ions on the Cr (VI) reducing activity of the biomass reported in this study.

Fig 6: Time-course of Cr (VI) decrease and Cr (III) production in solution with 1.0 mg L\(^{-1}\) Cr (VI). 100 rpm, 28°C, pH 4.0

Cr (VI) reducing capability has been described in some reports in the literature (Seng and Wang, 1994; Marsh, and McInerney, 2001; Sahin and Ozturk, 2005; Acosta et al., 2010; Aldrich et al., 2003; Fiol et al., 2008; Ramirez-Ramirez et al., 2004; Park et al., 2004b; Acosta et al., 2010; Cardenas-Gonzalez and Acosta-Rodriguez, 2011. Biosorption is the second mechanism by which the chromate concentration could be reduced, because the biomass shell can be regarded as a mosaic of different groups that could form coordination complexes with metals and our observations are like to the most of the reports in the literature (Seng and Wang, 1994; Marsh and McInerney, 2001; Sahin and Ozturk, 2005; Acosta et al., 2010; Aldrich et al., 2003; Fiol et al., 2008; Ramirez-Ramirez et al., 2004; Acosta et al., 2012; Cardenas-Gonzalez and Acosta-Rodriguez, 2011).
Removal of Cr (VI) in industrial wastes with Citrus limonium peel: We adapted a water-phase bioremediation assay to explore possible usefulness of *Litchi chinensis* Sonn peel, for eliminating Cr (VI) from industrial wastes, the biomass (5-10 g) was incubated with 20 and 50 g non-sterilized contaminated soil containing 297 mg Cr (VI)/g, suspended in trideionized water. It was observed that after five days of incubation with the biomass, the Cr (VI) concentration of soil sample decrease 100 and 98.14%, respectively (Fig. 7A) and the decrease level occurred without change significant in total Cr content, during the experiments. In the experiment carried out in the absence of the biomass, the Cr (VI) concentration of the soil samples decreased by about of 18% (date not shown); this might be caused by indigenous microflora and (or) reducing components present in the soil. We also performed a test of Cr (VI) bioremediation with the same contaminated soil using 5 g of different natural biomass and we found that litchi peel biomass was the most efficient (100% removal at 5 days of incubation), although the other biomasses tested too removal high metal concentrations of metal in a range of 95.2% for the fungus Paecelomyces sp and 84% for shrimp shell biomass, at the same incubation time (Fig. 7B). The chromium removal abilities of *Litchi chinensis* Sonn peel are equal or better than those of other reported biomass, for example tamarind peel (*Acosta et al.*, 2010), *Mammea americana* (*Acosta et al.*, 2010) *Candida maltose* RR1, (*Ramirez-Ramirez et al.*, 2004). In particular, this biomass was superior to the other biomass because it has the capacity for efficient chromium reduction under acidic conditions. Many of the Cr (VI) reduction studies were carried out at neutral pH (*Fukuda et al.*, 2008). Aspergillus niger also has the ability to reduce and adsorb Cr (VI) (*Fukuda et al.*, 2008). When the initial concentration of Cr (VI) was 500 ppm, *A. niger* mycelium removed 8.9 mg L⁻¹ of chromium/g dry weight of mycelium in 7 days.

Desorption of Cr (VI) by different solutions: Furthermore, we examined the ability of different solutions to desorb the metal bioadsorbed (250 mg L⁻¹) for the litchi biomass, obtaining high efficiency with 0.1 N NaOH and 0.5 N (80 and 61% respectively (Fig. 8)), which are less than reported for desorption of chromium (VI) with alkaline solutions (100%, pH = 9.5), 1.0 N NaOH (95%) and a hot solution of NaOH/Na₂CO₃ (90%), respectively, (*Singh et al.*, 2009; *Gupta and Babu*, 2009) and are higher than that reported (14.2%) using 0.2 M NaOH (*Wang et al.*, 2009). This indicates that binding of metal to biomass is not as strong and that it can be used up to 6-desorption cycles of removal, which further lowers the metal removal process of niches contaminated with it.

**CONCLUSION**

The *Litchi chinensis* Sonn peel biomass showed complete capacity of biosorption and reduction concentrations of 1.0 g L⁻¹ Cr (VI) in solution after 195 and 60 min of incubation, respectively, at 28°C, 100 rpm with 1 g of biomass. These results suggest the potential applicability of *Litchi chinensis* biomass for the remediation of Cr (VI) from polluted soils in the fields.

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