Research Paper

Fungal biomass supported on agricultural waste for industrial wastewater biosorption of hexavalent chromium (VI)

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ABSTRACT

This study reports the biosorption of hexavalent chromium [Cr(VI)] from industrial wastewater using fungal biomass supported on *Citrus × sinensis* peel or orange peel (OP). These agricultural wastes were evaluated as biosorbents as well as supports for *Penicillium sp.* and *Trichoderma* sp. biomass. The biosorbent dose, concentration of Cr(VI) and contact time effects on biosorption capacity of Cr(VI) ions was studied in batch model. The removal of Cr(VI) reached 85% for *Penicillium sp.* and 96% for *Trichoderma* sp., while *Citrus × sinensis* peel alone had 68% of removal. The Langmuir isotherm model fitted better to the obtained equilibrium data with a maximum adsorption capacity of 2.81 mg/g for *Penicillium sp.* and 9.85 mg/g for *Trichoderma* sp. Whereas *Citrus × sinensis* peel had 0.22 mg/g. Being pseudo-second order model which best described the biosorption kinetics for the three biosorbents. The result suggests that the three biosorbents represent a practical replacement for conventional process at low cost with efficient removal of hexavalent chromium [Cr(VI)] from industrial wastewater.

Keywords: Biosorption, chromium removal, kinetics; isotherms; *Penicillium sp.*; *Trichoderma* sp.

INTRODUCTION

Chromium release into the environment is the result of discharges from industrial activities such as leather tanning, mining, electroplating, metallurgy, pigments, battery manufacturing, fertilizers, petroleum refining, nuclear power production and wood preservation industries (Ye et al., 2010). The presence of chromium caused grave damage to ecosystems and human health. In nature, trivalent and hexavalent chromium are ecologically important because they are the most stable oxidation states of chromium (Vamkar and Bajpai, 2008). Hexavalent chromium [Cr(VI)] is very toxic and has been classified as group “A” carcinogen due to its mutagenic, teratogenic and carcinogenic nature (Evy et al., 2015). On the other hand, trivalent chromium [Cr(III)] is more stable than Cr(VI) being approximately 100 times less toxic and 1000 times less mutagenic (Morales-Barrera and Cristiani-Urbina, 2006). Furthermore, Cr(III) is an essential trace element necessary for glucose, lipid and amino-acid metabolism, as well as, popular dietary supplement (I-Son et al., 2013).

Many treatment processes like electrochemical method (electrocoagulation and electrodialysis), reverse osmosis, chemical precipitation, chemical reduction, membrane process, filtration, ion exchange, liquid extraction, evaporation, coagulation and adsorption are available for chromium removal (Nimmala et al., 2014). However, these technologies have significant disadvantages, such as less efficiency, the requirement of preliminary treatment steps, high operating costs and capital, high consumptions of reagent and energy and generation of toxic waste sludge in large quantities (Mishra and Doble, 2008).

In recent years, biosorbents have been considered as the cheapest, most abundant and environmentally friendly options. To date, a vast number of publications have been dedicated to the removal of heavy metals from wastewater...
using adsorption techniques with different low cost materials. One of the most studied groups of biosorbents are agricultural wastes (almond shell, apricot stone, banana peel, carrot residues, citrus peel, coconut shell, cornelian cherry, coffee dusts, jackfruit peel, grape waste, maple saw dust, maize cob, mango, orange peel, papaya wood, pine fruit, pomegranate peel, rice bran and husk, sugarcane bagasse, soya cake, tamarind seeds and tea waste). (I-Son et al., 2013; Nimmala et al., 2014; Pérez et al., 2009). Recently, biosorption a property in which inactive, live or dead biomasses are exploited for binding and concentrating metal of interest is from dilute aqueous solutions.

Biosorption of Cr(VI) mainly depends on the surface functional groups of microbial communities. Due to Cr(VI) contamination persistence, the search for efficient biosorbents continues. A variety of micro-organisms, bacteria, fungi, yeast and algae were isolated and screened for the cleanup of chromium from aqueous environments (Kumar et al., 2008). Among the micro-organisms, biomass from fungal strains of Aspergillus, Agaricus, Candida, Coriolus, Fusarium, Ganoderma, Lentinus, Mucor, Neurospora, Penicillium, Rhizopus, Rhizomucor, Saccharomyces, Trametes, Trichoderma and Yarrowia are the most frequently studied as biosorbents for chromium (Mishra and Doble, 2008; Kumar et al., 2008).

The three models for Cr(VI) biosorption are (Saha and Orvig, 2010):

Anionic adsorption: Negatively charged chromium species bind through electrostatic attraction to positively charged functional groups on the surface of biosorbents.

Adsorption-coupled reduction: Reduction of Cr(V) to Cr(III) by biomass in the presence of acid, in which a fraction of Cr(III) is adsorbed to the biomass.

Anionic and cationic adsorption: A proportion of Cr(V) is reduced to Cr(III) and the Cr(V) anionic and Cr(III) cationic are adsorbed to biomass.

It is well known that a high percentage of cell wall material (chitin, glucan, proteins and polymers which possess carboxyl, sulfhydryl, phosphoryl, hydroxyl, amino and imidazole functional groups at surface) possess outstanding metal binding properties (Pazouki et al., 2007; Prigione et al., 2009). Orange peels contain pectin, citrulline, cellulose and proteins; these polymers are rich in functional groups such as hydroxyl (cellulose) and carboxyl (pectin) and can easily bind metal ions. The chromium is removed from aqueous solutions through an adsorption mechanism in which the anionic chromate ion binds to positively charged groups (Nimmala et al., 2014; Pérez et al., 2009).

In the present study, two biomasses of fungus (Penicillium sp. and Trichoderma sp.) and Citrus × sinensis peel were used as biosorbents for the removal of Cr(VI) from industrial wastewater. The aim of the present investigation was to study different factors using a design factorial. Along with this, a detailed study was conducted for assessing the biosorption equilibrium employed in twelve different isotherm models and three sorption kinetics to studies for sorption of Cr(VI) by the three biosorbents.

MATERIALS AND METHODS

Preparation of the biosorbents

Orange peel (OP) were obtained from a local fruit market and washed under tap water several times followed by double distilled water. After thoroughly washing them, they were cut into small pieces and dried under sunlight for 7 days to remove moisture. The OP was added non-sterile in order to allow the omnipresent cosmopolite micro-organisms grow. In these research, the fungal species Penicillium sp. and Trichoderma sp. outgrew the other micro-organisms.

Systems and experimental techniques

A 3.15 mg Cr TOTAL/L solution was obtained for industrial wastewater. Batch experiments were conducted at room temperature in orbital shaker at 150 rpm using 100 ml Erlenmeyer flasks. The effect of different factors was evaluated with a 2^3 factorial design (5 repetitions in the central point) varying biosorbent dosage: only OP, OP used for support for Penicillium sp. (OP + Penicillium sp.) and OP used for support for Trichoderma sp. (OP + Trichoderma sp.)(2, 4 and 6 g/L), concentration of Cr (0.26, 1.57 and 3.15 mg/L) and time (1, 2 and 3 h) with the rest of the conditions kept constant in each parameter studies. The 1-ml samples were collected and filtered on a 0.45 µm membrane (HAWP cellulose esters; Millipore) at different time intervals. The filtrate was analyzed to determine the residual concentration of chromium (VI) by the spectrometric by 1-5 diphenylcarbazide method (APHA, 1998), the detection limit of this method is 0.1 mgCr/L and the calibration curve showed a linear correlation coefficient of R^2=0.999 for Cr(VI).

Biosorption kinetics

For these tests, 3.15 mg/L of Cr (VI) concentration of the industrial wastewater was used with 6 g/L of biosorbent dosage and only OP, OP + Penicillium sp. and OP + Trichoderma sp. was added to the Erlenmeyer flasks. Following this preparation, the suspensions were perfectly mixed on an orbital shaker at 250 rpm at a constant temperature of 25°C. At intervals of 15, 30, 60, 90, 120 and
180 min, 1 ml of the samples were collected and filtered through 0.45 µm membranes (Millipore brand, cellulose-esters, HAWP). The filtrate was analyzed to determine the residual chromium concentration by spectrophotometry. The kinetic studies were conducted in triplicate to determine the time needed to achieve equilibrium.

**Biosorption isotherms**

In these experiments, a 3.15 mg/L of Cr (VI) concentration of the industrial wastewater was used with 1, 2, 3, 4, 5 and 6 g/L of biosorbent dose (only OP, OP + *Penicillium* sp. and OP + *Trichoderma* sp.in each treatment), respectively. After the mixtures were prepared, the sample methodology used for the kinetic studies was applied in the same manner as the kinetic studies. The isotherms were also performed in triplicate.

**RESULTS AND DISCUSSION**

**Design experimental**

The statistical adsorption model for the three biosorbents for removal chromium: only orange peel (R²: 87.2), OP + *Penicillium* sp. (R²: 85.63) and OP + *Trichoderma* sp. (R²: 93.87) are shown in Equations 1 to 3 (non-significant terms are omitted):

% Removal Cr (OP): 43.15+20.25A-12.25B+14.75C  
(1)

% Removal Cr (VI) (OP + *Penicillium* sp.): 59.84+22.0C+20A+15.5AC  
(2)

% Removal Cr (VI) (OP + *Trichoderma* sp.): 70.23+24.75A+13.25C +11.25AC  
(3)

Where A: dose biosorbent, B: [Cr(VI)]₀, C: contact time.

Figure 1a, b and c presents the Pareto chart of standardized effects at p = 0.05. All the effects presented an absolute value higher than 2.3 (p = 0.05, indicated by the dashed line), were considered statistically significant.

**Biosorption kinetics**

The results from each of the biosorption kinetics were statistically analyzed, calculating the variance and standard deviation. Based on those two statistical
parameters, the model that best described the results of each experiment was determined out of three evaluated kinetics (pseudo-first order, pseudo-second order, and Elovich) (Table 1). Afterward, the constants of each equation and the equilibrium capacity \( (q_e) \) were calculated.

Table 2 shows the calculated values of the constants corresponding to each of the adsorption-kinetics models and equilibrium times. The model that best described the data for all the experiments was the pseudo-second order type, in which the removal mechanism involves covalent bonds that correspond to chemisorption. The chemisorption phenomenon can be described by pseudo-second order process.

### Adsorption isotherms

The results from the adsorption isotherms were used to estimate the constants of Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Harkins and Halsey isotherms were used in their linear form (Table 3).
Table 4: Biosorption isotherm of chromium using OP, OP + Penicillium sp., OP + Trichoderma sp. (n=21).

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>q_max (mg/g)</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange peel (OP)</td>
<td>0.22</td>
<td>0.66</td>
<td>0.9767</td>
</tr>
<tr>
<td>OP + Penicillium sp.</td>
<td>2.81</td>
<td>0.27</td>
<td>0.9904</td>
</tr>
<tr>
<td>OP + Trichoderma sp.</td>
<td>9.85</td>
<td>0.05</td>
<td>0.9956</td>
</tr>
</tbody>
</table>

Table 4 shows the isotherm constants and regression coefficient (R²) of the best model that described the experimental data for Cr(VI) biosorption on the three biosorbents. Langmuir isotherm was found to display the best fit among all the other two parameter isotherm models suggesting a monolayer mode of sorption with high R² using OP, OP + Penicillium sp. And OP + Trichoderma sp. The Langmuir isotherm assumes surface homogeneity such as equal availability of sorption sites and monolayer surface coverage. It is also based on the notion that no interaction takes place between the biosorbed Cr(VI) species.

Conclusions

In batch reactors, the three biosorbents can be used as efficient and economical sorbents for chromium (VI) because these agro industry wastes produced an effluent with a chromium (VI) concentration slightly lower than the value of criteria for agricultural water reuse in addition to a low water treatment cost with this biosorbents in comparison to commercial sorbents. Based on these results, the biosorption process with these three biosorbents shows higher feasibility with respect to commercial adsorbents for the removal of chromium (VI) in water.

REFERENCES


