UTILITY OF THE BIOMASS OF NEWSPAPER FOR THE ELIMINATION OF HEXAVALENT CHROMIUM REMOVAL FROM AQUEOUS SOLUTION

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ABSTRACT: We studied the Chromium (VI) removal capacity in aqueous solution by newspaper, using the diphenylcarbazide method to evaluate the metal concentration. So, the highest biosorption of the metal (50 mg/L) occurs within 24 hours, at pH of 1, and 28 °C. According to temperature, the highest removal was observed at 60 °C, in 5 hours, (100%). At the analyzed concentrations of Cr (VI), the newspaper showed good removal capacity, besides it removes efficiently the metal in situ (83.1%, and 93.9% of removal, 7 days of incubation, 5 g of biomass, in soil and water contaminated, respectively). So, it can be used to eliminate it from industrial wastewater.

KEYWORDS: Chromium (VI), newspaper, removal, wastewater, bioremediation

RESUMEN: Se estudió la capacidad de eliminación de Cromo (VI) en solución

acuosa mediante papel periódico, utilizando el método de la difenilcarbazida para evaluar la concentración del metal. Así, la mayor biosorción del metal (50 mg/L) se produce a las 24 horas, a un pH de 1 y a 28 °C. Con respect a la temperatura, la mayor remoción se observó a 60 °C, en 5 horas (100%). A las concentraciones de Cr (VI) analizadas, el papel periódico mostró buena capacidad de remoción, además elimina eficientemente el metal in situ (83,1% y 93,9% de remoción, a los 7 días de incubación y 5 g de biomasa, en suelo y agua contaminados, respectivamente), por lo que esta biomasa puede utilizarse para eliminarlo de las aguas residuales industriales.
PALABRAS CLAVE: Cromo (VI), Papel periódico, remoción, aguas residuales, biorremediación

1 I INTRODUCTION

Cr (VI) is a toxic metal and on the list of priority pollutants due to its mutagenic and carcinogenic properties defined by the US EPA (Environmental Protection Agency). Cr (VI) is mainly from electroplating, leather tanning, textile dyeing and metal finishing industries. The US EPA requires Cr (VI) in drinking water and inland surface waters is 0.05 and 0.1 mg/L, respectively (Kobya, 2004).

Conventional treatment technologies utilized in electroplating and metal finishing plants suffer from disadvantages such as high disposal and chemical costs and incomplete reduction of Cr (VI). Therefore, cost effective treatment technologies are needed to meet these requirements. Recently, a variety of low-cost materials have been studied for their ability to remove Cr (VI) from aqueous solution and promising results are shown. Among these low-cost adsorbents are dead microorganisms, clay minerals, agricultural wastes, industrial wastes and various other low-cost materials (Kamaludeen, et. al., 2003), like modified corn stalks, (Chen et. al., 2011), hazelnut shell (Cimino et. al., 2000), orange shell (Pérez- Marín et. al., 2007), tamarind shell (Acosta-Rodríguez et. al., 2010). It has also been reported that some of these biomasses can reduce chromium (VI) to chromium (III), like 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), Yohimbe bark (Fiol et. al., 2008), and litchii (Acosta-Rodríguez et. al., 2012).

Newspapers are complex materials and consist principally of cellulose which includes polar functional groups such as alcohols and ethers. These functional groups can be protonated at lower pH and therefore bind Cr (VI) by way of electrostatic interactions. In this study, newspapers were used for biosorption of Cr (VI) from aqueous solutions. Important factors affecting the biosorption, such as solution pH, adsorbent concentration, metal concentration, and reaction temperature were investigated.

2 I EXPERIMENTAL

2.1 Biosorbent used: Newspapers

The newspapers were cut into pieces (1 cm^2) and rind washed with water trideionized 72 hours under constant stirring, with water changes every 12 hours, and was used as biosorbent for the following experiments.

2.2 Methods

The stock solution was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) (AR grade) in trideionized water. The stock solution was finally diluted to obtain standard solutions. Solutions of 0.1 mol/L NaOH and/or HCl were used for pH adjustment. Batch adsorption experiments were carried out by shaking 1.0 g of sorbent with 100 mL aqueous solution of the desired concentration in a temperature-controlled water-batch shaker. Continuous mixing was provided during the experiments with a constant agitation speed of 150 rpm. Removal studies were carried out at constant pH 1.0, with initial concentration (50 mg/L) and adsorbent dose of 1.0 g/L at 28°C. After shaking, the solution samples were withdrawn at suitable time intervals. Effect of pH on the adsorption of Cr (VI) was studied by varying the pH from 1.0 to 4.0. The effect of temperature on adsorption equilibrium was studied by varying temperatures from 28 to 60°C. Effect of sorbent and metal concentration on uptake of Cr (VI) was investigated by varying the range of concentration from 1.0 to 5.0 g/L of sorbent, and 200 to 1000 mg/L of Cr (VI), respectively.

The resulting solution was centrifuged and the supernatant liquid analyzed. The concentrations of Cr (VI) were determined using Diphenylcarbazide method (Greenberg et. al., 1992). Diphenylcarbazide forms a red–violet complex selectively with Cr (VI), and the intensity of this complex was read at 540 nm using a UV–visible spectrophotometer.

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

3 I RESULTS AND DISCUSSIÓN

3.1 Effect of pH on adsorption

Figure 1 shows the effect of the incubation time and pH on Cr (VI) removal. The results indicate that the adsorption removal decreased from 81.15 to 0.0 % with increasing the pH from 1.0 to 4.0, suggesting that the removal was highly pH-dependent. The pH dependence of metal adsorption is largely related to the surface functional groups in the biosorbents and metal solution chemistry (Cheng et. al., 2002). As mentioned above, newspapers consist mainly of the cellulose, which contains polar functional groups, alcohols and ethers. These polar functional groups were protonated at lower pH and therefore the surface of the adsorbent positively charged. On the other hand, the Cr (VI) in the solution exists mainly in three oxidation states, i.e. $Cr_2O_7^{2-}$, $HCrO_4^{-}$, CrO_4^{2-}, the stability of these forms being dependent on the pH of the system. The dominant form of Cr (VI) is $HCrO^{4-}$ over the range of 1.0 < pH< 3.0, while CrO_4^{2-} is dominant in the range of pH > 4.0 (Kobya, 2004).

These results are like for tamarind shell (Acosta et al., 2010), but the most of authors report an optimum pH of 2.0 like Tamarind shell (Agarwal et. al., 2006), eucalyptus bark (Sarin and Pant, 2006), bagasse and sugarcane pulp, coconut fibers and wool (Dakiki et. al., 2002), for the tamarind shell treated with oxalic acid (Popuri et al., 2008), at pH of 2.0 and 5.0 for the mandarin bagasse (Zunbair et al., 2008), and almond green hull (Sharanavard et al., 2011).

3.2 Effect of temperature on adsorption

Temperature is found to be a critical parameter in the adsorption of Cr (VI) (Figure 2). The highest removal was observed at 60°C and 5 hours of incubation. At this point the total removal of the metal is carried out. The results are coincident for tamarind shell with 95% of removal at 58°C and 3 hours (Agarwal et. al., 2006), for the adsorption of cadmium (II) from aqueous solution on natural and oxidized corncob (40°C and 5 days) (Leyva-Ramos et. al., 2005), but this are different for the mandarin waste (Zunbair et al., 2008), *Caladium bicolor* (wild cocoyam) biomass (Jnr, and Spiff, 2005), and *Saccharomyces cerevisiae* (Ozer and Ozer, (2003). The increase in temperature increases the rate of removal of chromium (VI) and decreases the contact time required for complete removal of the metal, to increase the redox reaction rate (Agarwal et. al., 2006).

3.3 Effect of Initial Metal Concentration on adsorption

On the other hand, at high metal concentrations (1000 mg/L), biomass studied, shows the best results for removal, adsorbing 100% at 5 hours at 60°C, while 200 mg/mL of the metal are removed at 7 hours and 7 days, at 60°C and 28°C, respectively (Figures 3a, and 3b). The results are coincident for tamarind shell (Acosta-Rodríguez et. al., 2010; Agarwal et. al., 2006). With respect to other biomass used, most authors report lower removal efficiencies of metal, for example: 45 mg/L for eucalyptus bark (Sarin and Pant, 2006), 13.4 and 17.2 mg/L for bagasse and sugar cane pulp, 29 mg/L coconut fibers, 8.66 mg/L for wool (Dakiki et. al., 2002), 25 and 250 mg/L of chitin and chitosan (Sag, and Y. Aktay, 2002), and 1 mg/L for cellulose acetate (Arthanareeswaran et. al., 2002). The increase in initial concentration of Cr (VI), results in the increased uptake capacity and decreased % removal of Cr (VI). This was due to the increase in the number of ions competing for the available function's groups on the surface of biomass (Agarwal et. al., 2006).

3.4 Effect of sorbent dose on adsorption

To assess the influence of the adsorbent concentration on the Cr (VI) adsorption, adsorbent different concentrations were studied using solutions of 50 mg/L Cr (VI) at pH 1.0. As shown in Fig. 4, when the adsorbent concentration was increased from 1.0 to 5.0 g/L, also increases the removal of Cr (VI) in solution (100% of removal, with 4 and 5 g of biomass at 10 hours). This is likely due to the equilibrium concentration of the Cr (VI) in solution was lower in the presence of high adsorbent concentrations, and there are more sorption sites of the same, because the amount of added sorbent determines the number of binding sites available for metal sorption (Pócsi, 2011). Similar results have been reported for modified corn stalks (Chen et. al., 2011), tamarind shell (Acosta-Rodríguez et, al., 2010), and *Mucor hiemalis* and *Rhizopus nigricans*, although latter with 10 g of biomass (Tewari et. al., 2005; Bai and Abraham, 2001), but are different from those reported for biomass wastes from the mandarin (gabasse), whit an optimal concentration of biomass of 100 mg/L (Zubair et. al., 2008).

3.5 Removal of Cr (VI) in industrial wastes with newspaper

We adapted a water-phase bioremediation assay to explore possible usefulness of newspaper biomass for eliminating Cr (VI) from industrial wastes, the biomass was incubated with non-sterilized contaminated soil and water, containing 297 mg Cr (VI)/g, and 400 mg Cr (VI)/L, respectively, suspended in trideionized water. It was observed that after seven days of incubation with the biomass, the Cr (VI) concentration of soil and water samples decrease 90.1%, and 93.9%, respectively (Figure 5), and the decrease level occurred without change significant in total Cr content, during the assay. In the experiment carried out in the absence of the biomass, the Cr (VI) concentration of the soil and water samples decreased by about of 18% (date not shown); this might be caused by indigenous microflora and (or) reducing components present in the soil and water. The chromium removal abilities of newspaper biomass are equal than those of other reported biomass, for example tamarind shell (Acosta-Rodríguez et. al., 2010), *Mamea americana* shell (Acosta et. al., 2012), and *Candida maltose* RR1, (Ramírez-Ramírez et. al., 2004. 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 of chromium/g dry weight of mycelium in 7 days.

3.6 Desorption of Cr (VI) by different solutions

Furthermore, we examined the ability of different solutions to desorb the metal biosorbed (250 mg/L) for the newspaper biomass, obtaining very low efficiency with 0.1 N NaOH and 0.5 N (3.6% and 2.71% respectively, date not shown), 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 $NaOH/Na_2CO_3$ (90%), respectively, (Singh et. al., 2009; Gupta, and Babu, 2009), and using 0.2 M NaOH (Wang et. al., 2009). This indicates that binding of metal to biomass is strong and that it can be used one desorption cycles of removal.

4 | CONCLUSION

The newspaper biomass complete capacity showed of biosorption concentrations of 1.0 g/L Cr (VI) in solution after 7 days of incubation, at 28°C, 100 rpm with 1 g of biomass. These results suggest the potential applicability of newspaper biomass for the remediation of Cr (VI) from polluted soils and water in different places.

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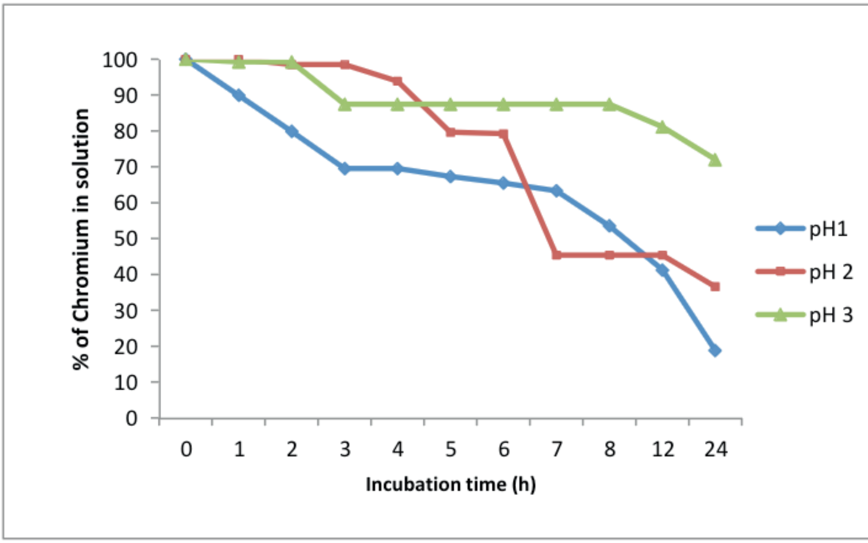

Figure 1: Effect of incubation time and pH on Chromium (VI) removal by newspaper.

50 mg/L Cr (VI), 100 rpm, 28ºC.

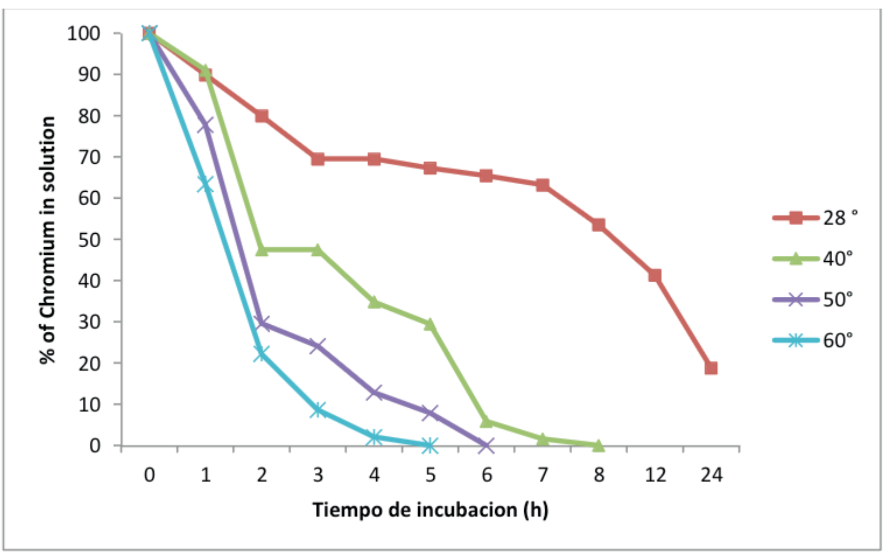

Figure 2: Effect of temperature on Chromium (VI) removal by newspaper.

50 mg/L Cr (VI), pH 1.0. 100 rpm.

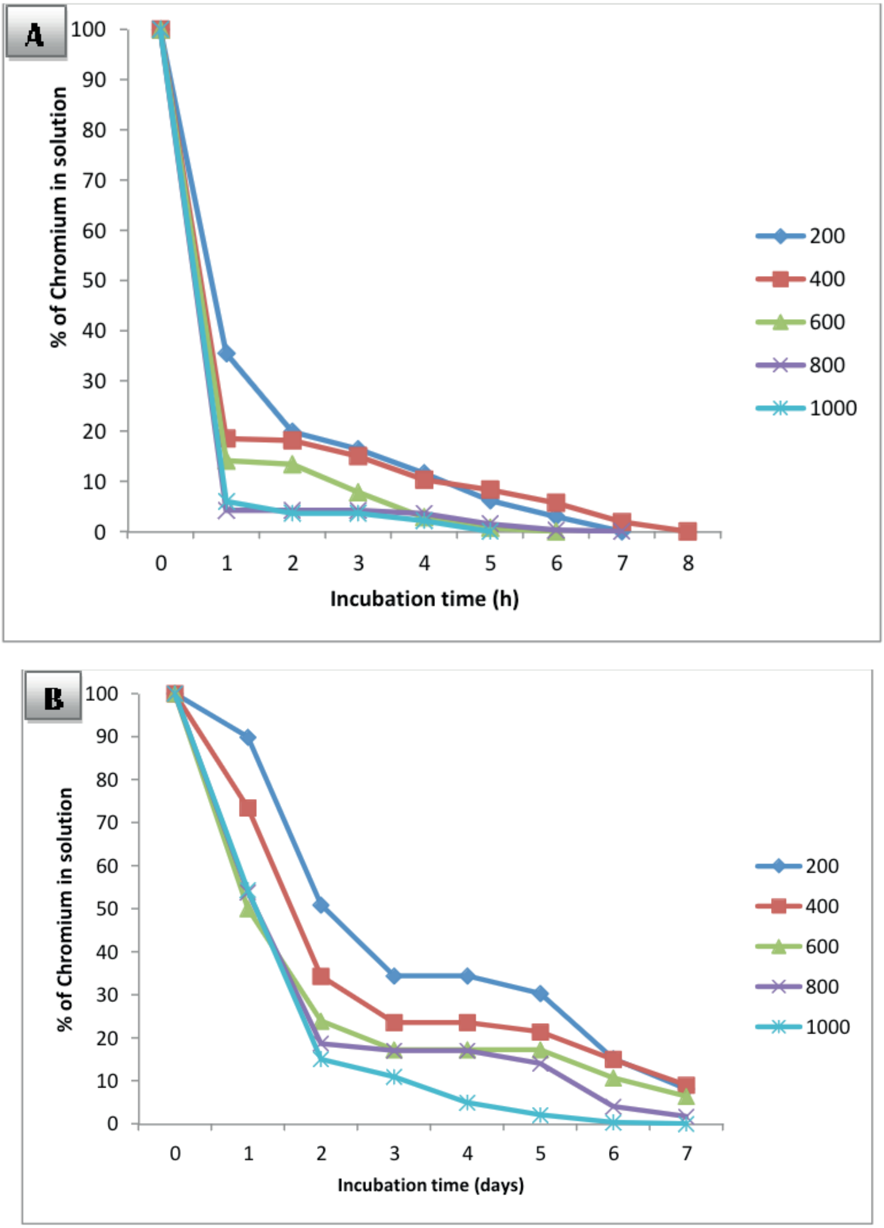

Figure 3: Effect of initial metal concentration on Chromium (VI) removal by newspaper.

pH 1.0. 100 rpm, A. - 60ºC, B. - 28ºC.

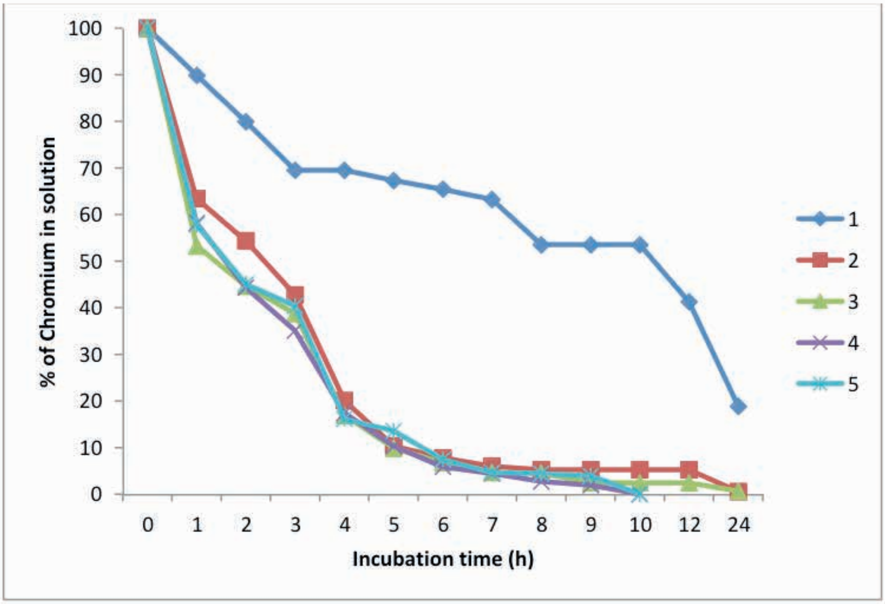

Figure 4: Effect of biomass concentration on the removal of 500 mg/L Cr (VI).

(60°C, pH= 1.0, 100 rpm).

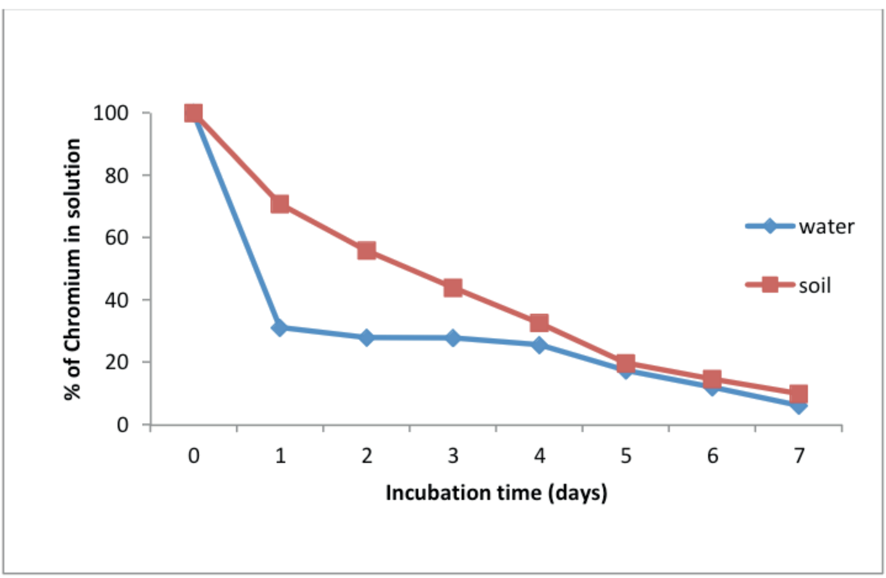

Figure 5: Removal of Chromium (VI) in industrial wastes incubated with the biomass.

100 rpm, 28ºC, of contaminated soil and water (297 mg Cr (VI)/g soil, and 400 mg/L Cr (VI).