

Hexavalent Chromium Removal from Aqueous Solution by *Mangifera indica* Shell

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Abstract

We studied the Chromium (VI) removal capacity in aqueous solution by the biomass of Mangifera indica shell, using the diphenylcarbazide method to evaluate the metal concentration. Therefore, the highest biosorption of the metal (50 mg/L) occurs within 70 seconds, at pH of 1.0, and 28°C, with 1 g of biomass. At the analyzed concentrations of Cr (VI), biomass showed good removal capacity, besides it removes efficiently the metal in situ (100% of removal, 6 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), Biomass of *M. indica*, Removal, wastewater, bioremediation

1. Introduction

Cr (VI) is a toxic metal, which belongs to a 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 maximum permissible limits by US EPA of Cr (VI) in drinking water and inland surface waters are 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, varieties 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 (Ahemad, 2014), like modified corn stalks,(Chen et. al., 2011),hazelnut shell(Cimino et. al., 2000),orange shell (Pérez- Marín et. al., 2007),litchi(Acosta-Rodríguez et. al., 2012).It has also been reported that some of these biomass 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),Yohimbebark (Fiol et. al., 2008), and *Citrus reticulata* shell (Acosta-Rodríguez et. al., 2013).

In this study, biomass of *M. indica* shell was used for biosorption of Cr (VI) from aqueous solutions. Important factors affecting the biosorption, such as solution pH, adsorbent concentration, and metal concentration were investigated.

2. Experimental

2.1 Biosorbent used: *M. indica* shell

The shell was obtained from the fruits harvested and offered in the marketplace Republic, between the months of May to July in 2013, in the capital city of San Luis Potosi, S.L.P. México. To obtain the biomass, the mango rind was washed with water trideionized 72 hours under constant stirring, with water changes every 12 hours. Subsequently, boiled 1 hour to remove traces of the fruit, which was dried at 80°C for 12 hours in the oven, ground in blender and stored in amber vials until use.

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 dilute to obtain standard solutions. Solutions of 0.1 mol/L NaOH and/or HCl were used for pH adjustment. Batch adsorption experiments were performed by shaking 1.0 g of sorbent with 100 mL aqueous solution of the desired concentration in a temperature-controlled with a water-batch shaker. Continuous mixing was provided during the experiments with a constant agitation speed of 120 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 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 Hexavalent Chromium and Trivalent Chromium were quantified by a spectrophotometric method employing diphenylcarbazide and chromazurol S, respectively (Greenberg et. al., 1992; Pantaler and Pulyaeva, 1985). Total Chromium was determined by electro thermal atomic absorptionspectroscopy (Greenberg et. al., 1992). The values shown in the results section are the mean from three experiments carried out by triplicate.

3. Results and Discussion

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 was full in the intervals of pH analyzed (from 1.0 to 4.0), in 70 second to 60 minutes, respectively, suggesting that the removal was highly pH-dependent. The pH dependence of metal adsorption is largely relate to the surface functional groups in the biosorbents and metal solution chemistry (Cheng et. al., 2002). *M. indica* shell contain carbohydrates, like of the hemicellulose (Guzman, et. al., 2013), 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 $pH > 4.0$ (Koby, 2004).

This results are like for *C. reticulata* shell (Acosta et al., 2013), 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 (Zubair et al., 2008), and almond green hull (Sharanavard et al., 2011).

3.2 Effect of Initial Metal Concentration on Adsorption

On the other hand, at low metal concentrations (200 mg/L), biomass studied showed the best results of removal, adsorbing 100% at 10 minutes at 28°C, while 800 and 1000 mg/mL of the metal are removed in 90 minutes (Figure 2). The results are coincident for litchi shell (Acosta-Rodríguez et al., 2012; Agarwal et al., 2006). With respect to other biomass used; most authors report lower removal efficiencies of metal with others biomass, 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 Aktay, 2002), and 1 mg/L for cellulose acetate (Arthanareeswaran et al., 2002). The increase of initial concentration of Cr (VI), results in the increased uptake capacity and decreased percentage of removal of Cr (VI). This was due to the increase in the number of ions competing for the available functions groups on the surface of biomass (Agarwal et al., 2006).

3.3 Effect of Sorbent dose on Adsorption

To assess the influence of the adsorbent concentration on the Cr (VI) adsorption, different adsorbent concentrations were studied using solutions of 1000 mg/L Cr (VI) at pH 1.0. As shown in Figure 3, 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 3, 4, and 5 g of biomass at 15 minutes). 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), mandarin shell (Acosta-Rodríguez et al., 2013), 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 mandarin (bagasse), with an optimal concentration of biomass of 100 mg/L (Zubair et al., 2008).

3.4 Time Course of Cr (VI) Decrease and Cr(III) Production

The ability of the *M. indica* shell to lower initial Cr(VI) of 1.0 g/L, and Cr(III) production in solution was analyzed. Figure 4 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).

Thus, after 1 hour of incubation, the shell biomass caused a drop in Cr(VI) from its initial concentration of 1.0 g/L to almost undetectable levels, and the decrease level occurred without change significant in total Chromium content. As expected, total Chromium concentration remained constant over time, in solution control. These observations indicate that *M. indica* shell is able to reduce Cr (VI) to Cr(III) in solution.

Furthermore, as the mandarin shell 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 (Smith et al., 2002; Seng and Wang 1994; Acosta et al., 2013; Xu et al., 2005, and Yong et al., 2005). There are three possible mechanisms by which chromate could be reduced to a lower toxic oxidation state (Ahmad, 2014): 1.- Under anaerobic conditions, numerous components of the cell's protoplasm such as amino acids, nucleotides, carbohydrates, vitamins, organic acids, glutathione, hydrogen NADH (NADPH in some species), flavoproteins, and hemoproteins, which act as electron donors, reduce Cr (VI) which serves as terminal electron acceptor. 2.- Soluble reductases: under aerobic conditions, NAD(P)H dependent extracellular soluble reductases are produced purposely by the cell to reduce Cr (VI) to Cr (III) that is removed by reacting with functional groups present on cell surface, and 3.- Membrane-associated reductases: anaerobic Cr (VI) reduction generally involves membrane-associated reductases which sometimes require H₂ or glucose as electron donors (Ibrahim et al. 2012). Moreover, anaerobic Cr (VI) reduction wherein Cr (VI) acts as an electron acceptor in the electron transport chain is also reported (Wang 2000; Quintana et al. 2001). 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 ionson the Cr(VI) reducing activity of the biomass reported in this study.

3.5 Removal of Cr(VI) in Industrial Wastes with Biomass of *M. indica* Shell

We adapted a water-phase bioremediation assay to explore possible usefulness of this biomass for eliminating Cr (VI) from industrial wastes. The biomass was incubated with no sterilized contaminated soil and water, containing 297 mg Cr(VI)/g, and 175 mg Cr (VI)/L, respectively, suspended in trideionized water. It was observed that after six days of incubation with the biomass, the Cr(VI) concentration of soil and water samples decrease 100% in both (Figure 5), and the decrease level occurred without change significant in total Chromium 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 micro flora and (or) reducing components present in the soil and water. The chromium removal abilities of *M. indica* biomass are equal than those of other reported biomass, for example litchi shell (Acosta et. al., 2012), *C. reticulata* shell (Acosta-Rodríguez, et. al., 2013) 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) of the *M. indicabiomass*, obtaining very low efficiency with 0.1 N NaOH and 0.5 N (66.3% and 70.4%, respectively (Figure 6), 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 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.

4.0 Conclusion

The *M. indica* shell biomass complete capacity showed of biosorption concentrations of 1.0 g/L Cr(VI) in solution after 90 minutes of incubation, at 28°C, 100 rpm with 1 g of biomass. These results suggest the potential applicability of this biomass for the remediation of Cr(VI) from polluted soils and water in different places.

5.0 References

- Acosta-Rodríguez, I., Coronado-Quintero, E., Cárdenas-González, J.F., Tovar-Oviedo, J. and Martínez-Juárez, V.M. (2012). Hexavalent Chromium Removal by *Citrus reticulata* shell. *Journal of Natural Sciences* 1(1), 29-39.
- Acosta-Rodríguez, I., Martínez-Pérez, R., Cárdenas-González, J.F., Moctezuma-Zárate, M.G. and Martínez-Juárez, V.M. (2012). Hexavalent Chromium Removal by *Litchi chinensis* Sonn Peel. *American Journal of Biochemistry and Biotechnology*. 8 (1), 7-13.
- Agarwal, G.S., Kumar, H., and Chaudari, S. (2006). Biosorption of aqueous chromium (VI) by *Tamarindus indicaseeds*. *Bioresource Technology*. 97, 949-956.
- Ahemad, M. (2014). Bacterial mechanisms for Cr(VI) resistance and reduction: an overview and recent advances. *Folia Microbiologica*. 59, 321–332.
- Arthanareeswaran, G., Thanikaivelan, P., Jaya, N., Mohan, D., and Raajenthiren, M. (2002). Removal of chromium from aqueous solution using cellulose acetate and sulfonated poly(ether ketone) blend ultrafiltration membranes. *Biochemical Engineering Journal*. 12, 43-153.
- Bai, R.S. and Abraham, T.E. (2001). Biosorption of chromium (VI) from aqueous solution by *Rhizopus nigricans*. *Bioresource Technology*, 79, 73-81.
- Chen, J.P., Hong, L., Wu, S.N., and Wang, L. (2002). Elucidation of interactions between metal ions and calcium alginate based ion exchange resin by spectroscopy analysis and model simulation. *Langmuir* 18, 9413–9421.
- Chen, S., Yue, Q., Gao, B., Li, Q., and Xu, X. (2011). Removal of Cr(VI) from aqueous solution using modified corn stalks: Characteristic, equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal*. 168, 909-917.

- Cimino, G., Passerini, A., and Toscano, G. (2000). Removal of toxic cations and Cr(VI) from aqueous solution by *Halzelnut shell*. *Water Research*. 34 (11), 2955-2962.
- Dakiki, M., Khamis, M., Manassra, A., and Mer'eb, M. (2002). Selective adsorption of chromium (VI) in industrial wastewater using low cost abundantly adsorbents. *Advances Environmental Research*, 6, 533-540.
- Fukuda, T., Ishino, Y., Ogawa, A., Tsutsumi, K., and Morita, H. (2008). Cr(VI) reduction from contaminated soils by *Aspergillus* sp. N2 and *Penicillium* sp. N3 isolated from chromium deposits. *Journal of General and Applied Microbiology*. 54, 295-303.
- Greenberg, A.E., Clesceri, L.S., and Eaton, A.D. (1992). Standard methods for the examination of water and wastewater. 18^a ed. American Public Health Association. (pp. 58-3.60, 187-190). Washington, D.C.
- Gupta, S., and Babu, B.V. (2009). Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chemical Engineering Journal*. 150, 352-365.
- Guzman, O., Lemus, C., Bugarin, J., Bonilla, J. and Ly, J. (2013). Composición y características químicas de mangos (*Mangifera indica* L.) destinados a la alimentación animal en Nayarit, México. *Revista Cubana de Ciencia Agrícola*, Tomo 47, Número 3, 273-277.
- Ibrahim, A.S.S., Elbadawi, Y.B., El-Tayeb, M.A. and Al-Salamah, A.A. (2012). Hexavalent chromium reduction by novel chromate resistant alkaline *Bacillus* sp., strain KSUCr9a. *African Journal of Biotechnology*. 11, 3832-3841.
- Kamaludeen, S.P.B., Megharaj, M., Juhasz, A.L., Sethunathan, N., and Naidu, R. (2003). Chromium-Microorganism Interactions in Soils: Remediation Implications. *Review Environmental Contamination Toxicology*. 178, 93-164.
- Koby, M. (2004). Adsorption, Kinetic and Equilibrium Studies of Cr(VI) by Hazelnut Shell Activated Carbon. *Adsorption Science and Technology*. 22 (1), 51-64.
- Pantaler, R.P. & Pulyaeva, I.V. (1985). A spectrophotometric study of complexation between chromium and chromazurol S. *Journal of Analytical Chemistry (Moscow)*. 40, 1634-1639.
- Pérez-Marín, A.B., Meseguer, V., Zapata, J.F., Ortuño, M., Aguilar, J., Sáez S., and Lloréns, M. (2007). Removal of cadmium from aqueous solutions by adsorption onto orange waste. *J. Hazardous Materials*. 139, 122-131.
- Pócsi, I. (2011). Toxic Metal/Metalloid Tolerance in Fungi. A Biotechnology-Oriented Approach. Bánfalvi, G. (ed.), *Cellular Effects of Heavy Metals* (pp. 31-58). Springer Science.
- Popuri, R.S., Jammala, A., Naga Suresh, K., and Abuburi, K. (2007). Biosorption of hexavalent chromium using tamarind (*Tamarindus indica*) fruit shell-a comparative study. *Journal of Biotechnology*, 10 (3), 358-367.
- Quintana, M., Curutchet, G. and Donati, E. (2001) Factors affecting chromium(VI) reduction by *Thiobacillus ferrooxidans*. *Biochemical Engineering Journal*. 9:11-15.
- Ramírez-Ramírez, R., Calvo-Méndez, C., Avila-Rodríguez, M., Lappe, P., Ulloa, M., Vázquez-Juárez, R., and Gutiérrez-Corona, J.F. (2004). Cr(VI) reduction in a Chromate-resistant strain of *Candida maltose* isolated from the leather industry. *Antonie van Leeuwenhoek*. 85, 63-68.
- Razmovski, N.R.N. and Sciban, M.B. (2007). Effect of different conditions on Cu(II) and Cr(VI) biosorption by dried waste tea fungal biomass. *APTEFF*, 38, 1-19.
- Sag, Y. and Aktay, Y. (2002). Kinetic studies on sorption of Cr (VI) and CU (II) ions by chitin, chitosan and *Rhizopus arrhizus*. *Biochemical Engineering Journal*. 12, 143-153.
- Sarin, V. and Pant, K.K. (2006). Removal of chromium from industrial waste by using eucalyptus bark. *Bioresource Technology*, 97, 15-20.
- Seng, H. and Wang, Y.T. (1994). Biological reduction of chromium by *E. coli*. *Journal of Environmental Engineering*. 120, 560-572.
- Shafqat, F., Bhatti, H.N., Hanif, M.A., and Zubair, A. (2008). Kinetic and equilibrium studies of Cr(III) and Cr(VI) sorption from aqueous solution using rosagrass an teplitz (*Red rose*) waste biomass. *Journal Chile Chemistry Society*, 53 (4), 1667-1672.
- Sharanavard, M., Ahmadpourand, A., and Reza Doosti, M. (2011). Biosorption of Hexavalent Chromium Ions from Aqueous Solutions using Almond Green Hull as a Low-Cost Biosorbent. *European Journal of Scientific Research*. 58 (3), 392-400.
- Singh, K.K., Hasan, S.H., Talat, M., Singh, V.K., and Gangwar, S.K. (2009). Removal of Cr (VI) from aqueous solutions using wheat bran. *Chemical Engineering Journal*. 151, 113-121.

Smith, W.A., Apel, W.A., Petersen, J.N., and Peyton, B.M. (2002). Effect of carbon and energy source on bacterial chromate reduction. *Bioremediation Journal*. 6, 205-215.

Tewari, N., Vasudevan, P., and Guha, B. (2005). Study on biosorption of Cr(VI) by *Mucorhiemalis*. *Biochemical Engineering Journal*. 23, 185-192.

Wang, Y.T. (2000) Microbial reduction of chromate. In: Lovley DR (ed). *Environmental microbe-metal interactions*. American Society for Microbiology Press, Washington DC

Wang, X.S., Tang, Y.P., and Tao, S.R. (2009). Kinetics, equilibrium and thermodynamic study on removal of Cr (VI) from aqueous solutions using low-cost adsorbent Alligator weed. *Chemical Engineering Journal*. 148, 217-225.

Xu, X. R., Li, H.B., Gu, J.D., and Li, X. Y. (2005). Kinetics of the reduction of Chromium (VI) by Vitamin C. *Environmental Toxicology and Chemistry*. 24 (6), 1310-1314.

Yong, L., Xin-Hua; X., and Ping, H. (2005). Remediation of Cr (VI) in solution using vitamin C. *Journal of Zhejiang University Science*. 6B, (6), 540-542.

Zubair, A., Bhatti, H.N., Hanif, M.A., and Shafqat, F. (2008). Kinetic and equilibrium modeling for Cr (III) and Cr (VI) removal from aqueous solutions by *Citrus reticulata* waste biomass. *Water Air Soil Pollution*. 191, 305-318.

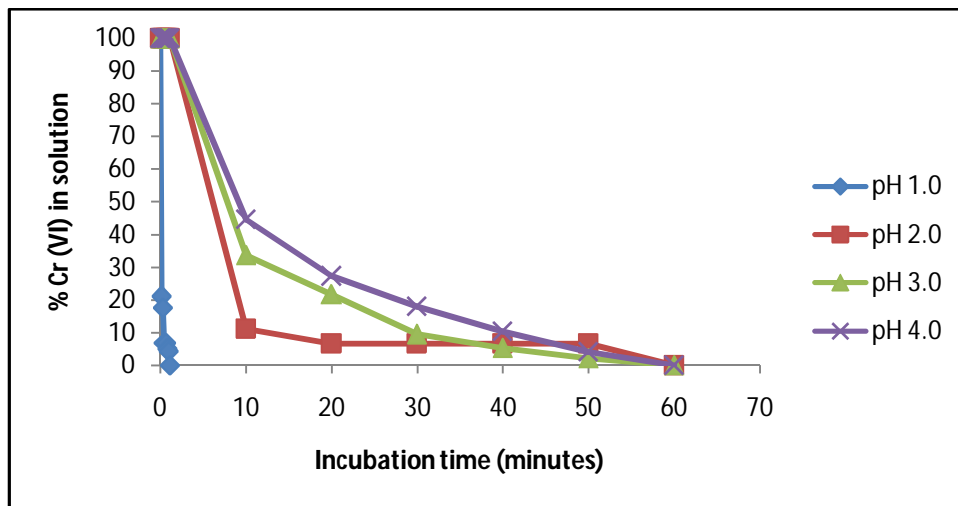


Figure 1: Effect of Incubation Time and pH on Chromium (VI) removal by the Biomass of *M. Indica* shell. 50 mg/L Cr (VI), 100 rpm, 28°C

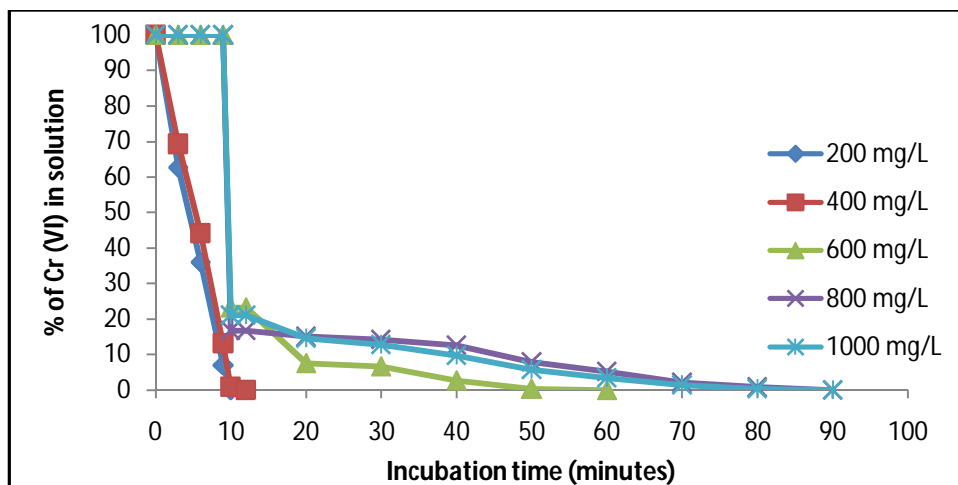


Figure 2: Effect of Initial Metal Concentration on Chromium (VI) Removal by the Biomass of *M. Indica* Shell. pH 1.0. 100 rpm. 28°C

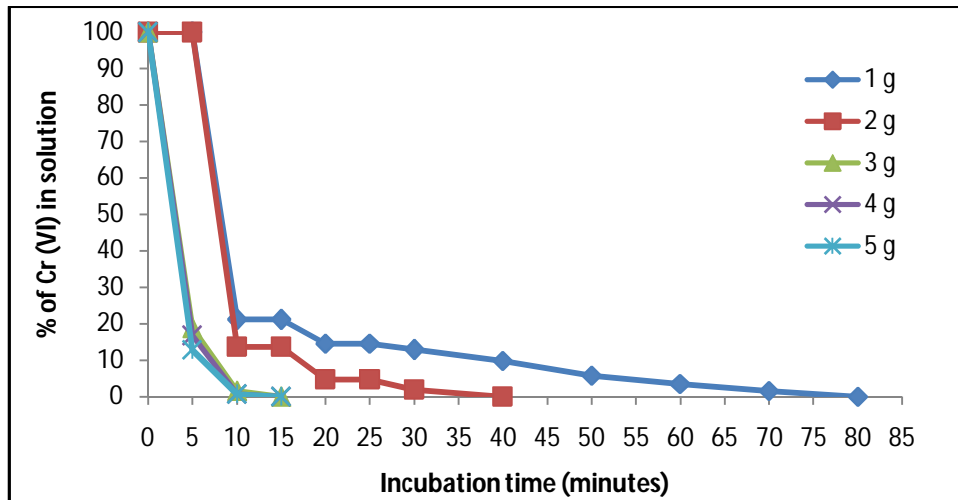


Figure 3: Effect of Biomass Concentration on the Removal of Different Concentrations of Cr (VI). 28°C, pH= 1.0, 100 rpm

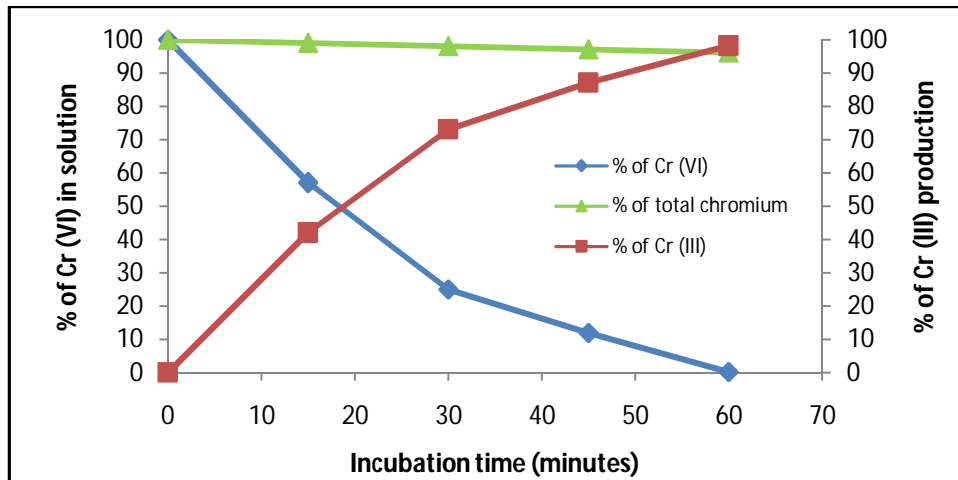


Figure 4: Time-Course of Cr (VI) Decrease and Cr (III) Production in Solution with 1.0 g/L Cr (VI). 100 rpm. pH 1.0. 28°C

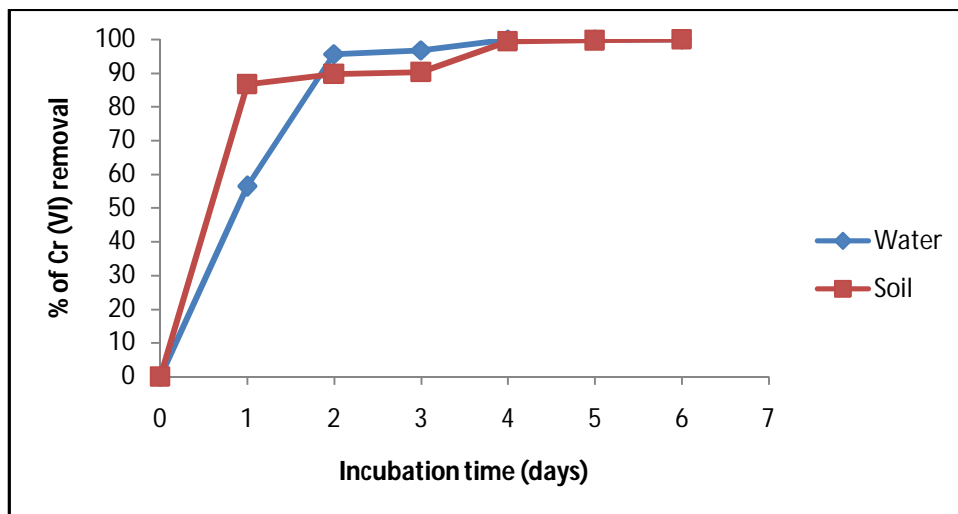


Figure 5: Removal of Chromium (VI) in Contaminated Soil and Water (297 mg Cr (VI)/g soil, and 175 mg/L Cr (VI). 5 g of biomass. 100 rpm. 28°C

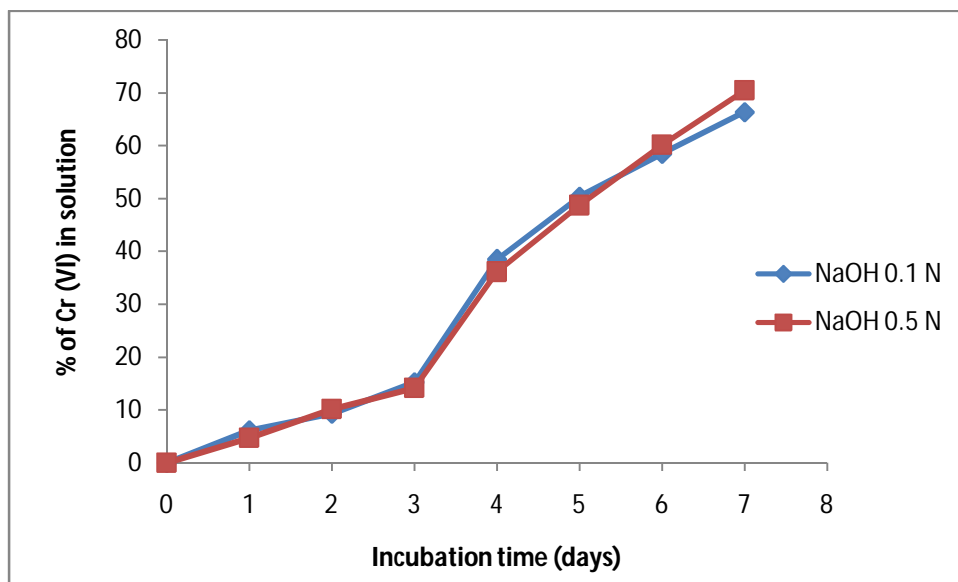


Figure 6: Desorption of Chromium (VI) (250 mg/L) by Different Solutions(1 g of Biomass. 28°C, 100 rpm).