BEST: International Journal of Management Information Technology and Engineering (BEST: IJMITE)
ISSN (P): 2348-0513, ISSN (E): 2454-471X
Vol. 6, Issue 9, Sep 2018, 1-10

EVALUATING THE EFFECTIVENESS OF CHITOSAN FOR REMOVAL OF HEXAVALENT CHROMIUM FROM WASTEWATER

DANADHI GUNAWARDANA & SANJA GUNAWARDENA
Department of Chemical and Process Engineering University of Moratuwa, Sri Lanka

ABSTRACT

Chitosan is a natural biopolymer which is considered as a promising adsorbent to remove heavy metals from wastewater due to its good adsorption properties, low toxicity, and availability. Identification and analysis of the factors affecting the removal of hexavalent chromium using chitosan are vital for the treatment of Cr containing industrial effluents. Main factors which affect removal efficiency include effluent Cr concentration, chitosan loading, mode of operation, pH and presence of other ions. Results of this study show that Chitosan can efficiently remove Cr (VI) at low Cr concentrations, showing higher adsorption capacity than most other natural adsorbents. A study on adsorption kinetics using Langmuir and Freundlich isotherms showed that the acquired data fit better with Freundlich isotherm. Higher adsorption capacities were observed at acidic pH, which can be attributed to the protonation of amine groups. Presence of Cl ions was shown to have a negative impact on adsorption efficiency

KEYWORDS: Adsorption, Chitosan, Chromium (VI); Equilibrium & Kinetics

INTRODUCTION

Chromium (Cr) can be present in aqueous media in the forms of Cr (III) and Cr (VI). Cr (VI) is widely present in the waste streams of metallurgical industry and refractory industry while Cr (III) is present in the effluents of the tannery, textile and decorative plating industries (Kotaś & Stasicka, 2000). Chromium is considered one of the most hazardous pollutants in industrial wastewater streams due to its toxic nature. Hexavalent Chromium [Cr (VI)] is listed as a known carcinogen and also can cause other adverse health effects such as kidney and liver damage and nasal, skin and eye irritation and ulceration ("Hexavalent Chromium," 2015). Conventional methods of Chromium removal from wastewater include chemical precipitation, membrane filtration, ion exchange, and magnetic separation. These methodologies give inherent problems such as sludge formation, high cost and inability to achieve the required level of removal efficiency (Bhaumik, Setshedi, Maity, & Onyango, 2013; Chu & Hashim, 2007; Hu, Chen, & Lo, 2005).

Use of different biomass as adsorbents to remove metal ions from water has been researched and published (Owlad, Aroua, Daud, & Baroutian, 2009). Adsorbents which have shown good chromium removal properties include olive pomace, sawdust, coconut shells and hazelnut shells (Malkoc, Nuhoglu, & Dundar, 2006; Owlad et al., 2009). Hazelnut shells have shown up to 99% of Chromium ion removal under acidic conditions (Owlad et al., 2009).

Chitosan, a natural biopolymer which is commonly found in exoskeletons of invertebrates or cell walls of most fungi has shown promising results as an adsorbent (Rhazi et al., 2002). Chitosan can easily be produced by alkaline deacetylation of chitin. The metal adsorbing ability of chitosan arises due to the presence of free amine groups which enables it to chelate the ions of transition metals. Metal ions which have shown highest affinity for chitosan are Cu^{2+}, Hg^{2+},

Zn^{2+} and Cd^{2+}(Rhazi et al., 2002). Previous researches have also shown that chitosan can be used as a potential adsorbent for the removal of Cr and among the two forms of chromium, Cr (VI) is shown to have a higher affinity for chitosan than Cr (III) (Maruca, Suder, & Wightman, 1982; Ngah, Kamari, Fatinathan, & Ng, 2006; Udaybhaskar, Iyengar, & Rao, 1990). It has also been shown that the adsorbed chitosan can effectively be desorbed using HNO_3 and EDTA, thus making it a reusable adsorbent (Ngah et al., 2006).

Most of the previous research on chitosan batch adsorption have focused on identifying the optimum conditions and characterizing the adsorption behavior. However, in industrial applications of chitosan as an adsorbent, multiple factors have to be considered including the method of adsorption (batch or packed-bed), particles size of chitosan, a range of pollutant concentration, an effect of pH and presence of various ions in the solution. In this research, a comprehensive study on the removal of Cr (VI) from a solution using chitosan as an adsorbent was carried in the batch operation. Further, analysis of adsorption behavior, determination of the effects of Cr (VI) concentration, pH and other ions on adsorption was investigated.

MATERIALS AND METHODOLOGY

Materials

Waste shrimp shells which were used as the raw material to produce chitosan were collected from restaurants. 1,5-diphenylcarbazide (Sigma Aldrich) was of analytical grade and all other chemicals were of laboratory grade.

Preparation of Adsorbent

Preparation of chitosan was based on a previous research (Mendis et. al 2017). Firstly, shrimp shells were washed with hot water to remove residual meat and other impurities and then dried at 105 ^{0}C. Dried shrimp shells were ground to a particle size less than 250 µm. Ground shells were demineralized by treating with 0.25 M hydrochloric acid solution for 15 minutes at room temperature and deproteinized by treating with 1 M sodium hydroxide solution for 24 hours at 70 ºC. Decoloration was achieved by treating first with hot ethanol and then with boiling acetone and the resulting product was deacetylized by treating with a 45% sodium hydroxide solution at 105 ºCfor 7 hours.

Batch Experiments

2 g of chitosan was added to 2 L of chromium solutions of selected concentrations and kept stirring at the 30^{0}C temperature at selected pH. Solution pH was adjusted using 1 M HCl and 2 M NaOH. 1 ml of the solution was withdrawn using a pipette in 5 min intervals and analyzed for Cr (VI) concentration. Equilibrium curves were obtained by plotting the residual chromium concentration against time. Since equilibrium was reached before 2 hours of operation for solutions having 0.1, 0.5 and 1 mg/L Cr concentrations, for all the experiments reaction time was limited to 2 hours. Effect of Cl ion concentration on the removal of Cr was studied by varying NaCl concentration while maintaining Cr (VI) concentration at 1 mg/mL.

DETERMINATION OF CHROMIUM ION CONCENTRATION

Chromium ion concentration was determined using UV-visible spectrophotometry, based on the formation of the purple colored complex between Cr (VI) and 1,5-diphenylcarbazide(Balasubramanian & Pugalenthi, 1999). 1 ml of Chromium solution was withdrawn to a volumetric flask and 3 ml of 6 N sulfuric acid solution and 2 ml of 1,5-diphenylcarbazide solution (prepared by dissolving 250 mg of 1,5-diphenylcarbazide in 100 ml of acetone) was added. The solution was diluted up to 50 ml using distilled water and shaken thoroughly for fullcolor development. The Color was measured at a UV-visible spectrophotometer (SHIMADZU UV-1800 Model) at 540 nm. At higher Chromium concentrations, the extracted samples were diluted in order to maintain the absorbance in the linear range.

RESULTS AND DISCUSSIONS

Characterization of Chitosan

FTIR spectrum can be used to determine the Degree of Deacetylization (DDA) of chitin to chitosan and Figure 1 shows the FTIR spectrum of the chitosan prepared in this study. A degree of deacetylization can be calculated using equation (1)(Baxter, Dillon, Anthony Taylor, & Roberts, 1992).

$$(A_{1655}/A_{3450}) \text{ x } 115\% \tag{1}$$

DDA is a measure of the content of amine groups in the molecular chain. It is reported that DDA has a great effect on physiochemical properties of chitosan such as hydrophilicity, crystallinity, degradation, and bio-compatibility (Yuan, Chesnutt, Haggard, & Bumgardner, 2011). Under acidic conditions, amine groups in Chitosan can protonate, increasing the polyelectrolyte charge which strongly affects molecular structure and intermolecular interactions. As a result, deacetylation provides more sites for adsorption and hence makes chitosan a better adsorbent(He et al., 2016; Singh & Nagendran, 2016). DDA of prepared chitosan sample was 92% which indicates that more acetyl groups have been removed and amino acid groups have been exposed.

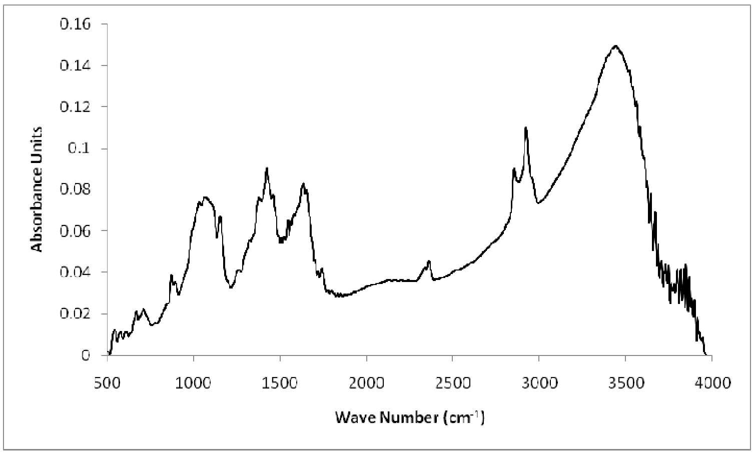
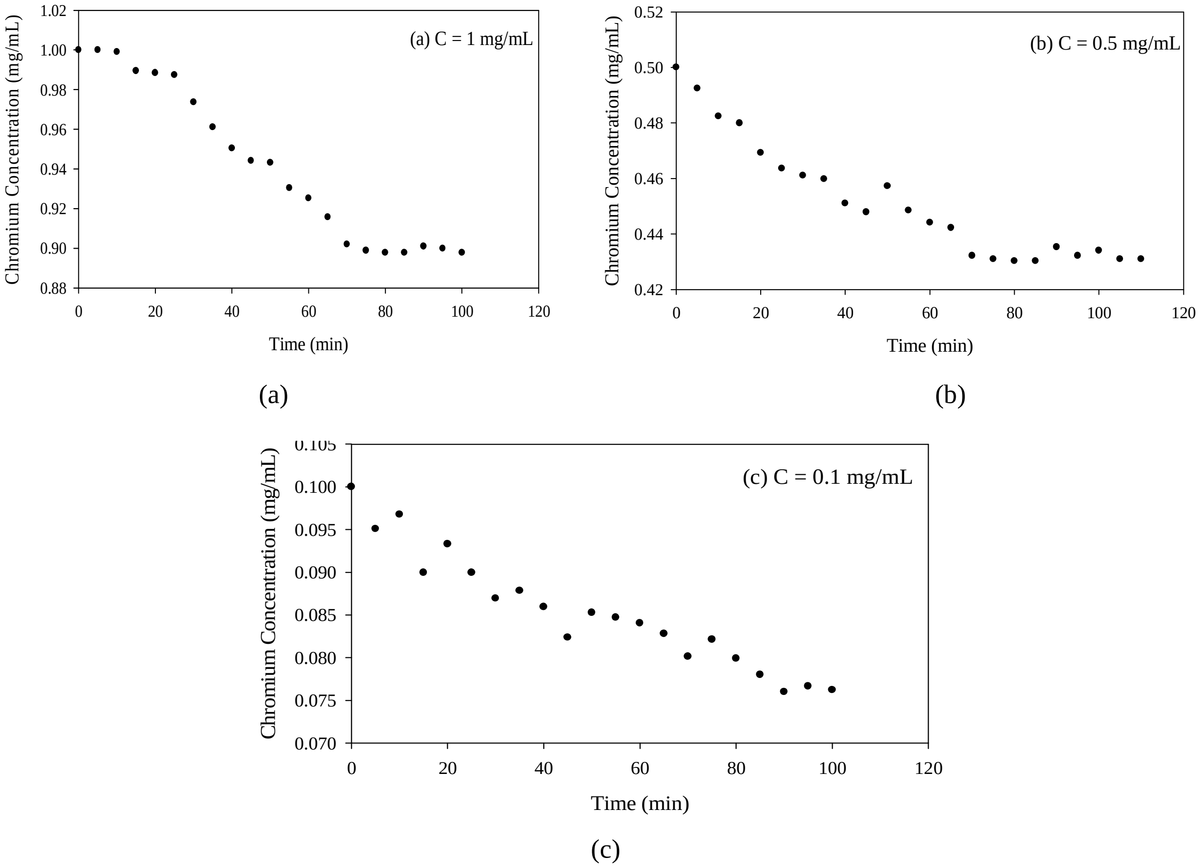


Figure 1: FTIR Spectrum for Prepared Chitosan

Equilibrium Curves

Equilibrium curves obtained for the adsorption of Cr from 1, 0.5 and 0.1 g/L solutions using chitosan are given in Figure 2 (a-c)


(a) (b)

(c)

Figure 2 - Equilibrium Curves at Chromium Concentrations of (a) 1 mg/mL, (b) 0.5 mg/mL (c) 0.1 mg/mL at 30 ^{0}C Temperature and 5.0 pH. Equilibrium is Achieved within a Shorter Time for Higher Cr (VI) Concentrations

As seen from equilibrium curves, all three systems reached equilibrium before 2 hr at all chromium concentrations. Higher the chromium concentration shorter the time required to reach the equilibrium. At higher chromium concentrations there are more interactions between chitosan particles and chromium ions, leading to faster adsorption rates.

Equilibrium capacity can be determined using equation (2)

$$Q = \frac{(C_0 - C_e)V}{w} \qquad (2)$$

Where C_0 and C_e are initial and final chromium concentration (mg/ml), V is the volume of solution (ml) and w is the weight of chitosan (mg)

The equilibrium capacities at each of these conditions are given in Table 1.

Table 1: Percentage removal and Equilibrium Adsorption Capacities at Three Different Chromium Concentrations

Chromium Concentration (mg/ml)	Percentage Removal (%)	Chromium uptake Capacity (g Chromium/g Chitosan)
0.1	23.77	0.024
0.5	13.82	0.069
1.0	10.22	0.102

According to Table 1, uptake capacity was increased when the chromium concentration was increased while the percentage removal of chromium was decreased. This behavior is explicable because more chromium ions can attach to chitosan particles when the ion concentration is high. However, at higher Cr (VI) concentrations, chitosan particles get saturated fast reducing the percentage removal.

The previous study on packed bed adsorption to remove chromium ions using chitosan showed adsorption capacities of 0.062 g/g, 0.088 g/g and 0.189 g/g at chromium ion concentrations of 0.1, 0.5 and 1.0 mg/ml respectively (Mendis et al., 2017). These data imply that packed bed adsorption is significantly more effective than batch adsorption. However, in batch adsorption, treated wastewater has uniform quality, while in packed-bed adsorption the effluent water quality varies as the bed gets saturated.

The maximum adsorption capacity of chitosan is higher than most reported adsorbents including sawdust, sugar cane bagasse, coconut husks and eucalyptus bark (Sarin & Pant, 2006). The highest removal efficiency of Cr (VI) ions is reported for activated carbon (Arris & Lehocine, 2014; Sarin & Pant, 2006). However, compared to activated carbon, chitosan is less toxic and can be easily produced using natural resources. Therefore, chitosan can be considered as an effective adsorbent to remove chromium ions from wastewater.

EFFECT OF CHROMIUM CONCENTRATION

Variation of chromium uptake capacity with various initial chromium concentrations is shown in Figure 3. As seen in Figure 3, a steady increase of chromium uptake capacity can be observed with increasing chromium concentration. However, a variation of chromium uptake capacity with concentration is non-linear and the gradient of the curve tends to decrease at higher chromium concentrations. This may be a result of saturation of active sites in chitosan with chromium ions. Therefore, removal of chromium using chitosan would be most efficient if chromium concentration is maintained at values less than 0.5 g/L. Since the chromium concentration in most industrial wastewaters lies within the range of 0.01 g/L - 0.5 g/L, chitosan can be used effectively for chromium removal in most industrial applications (Dhungana & Yadav, 2009).

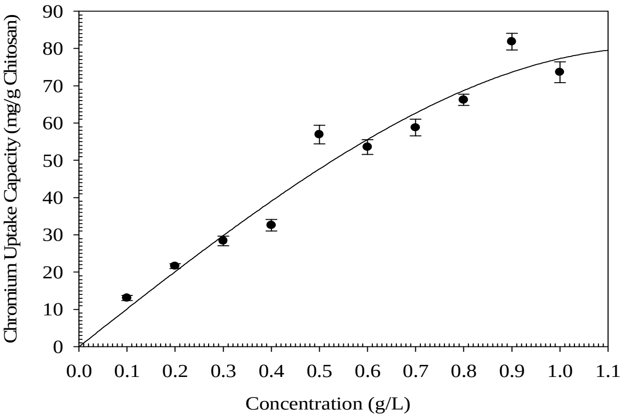
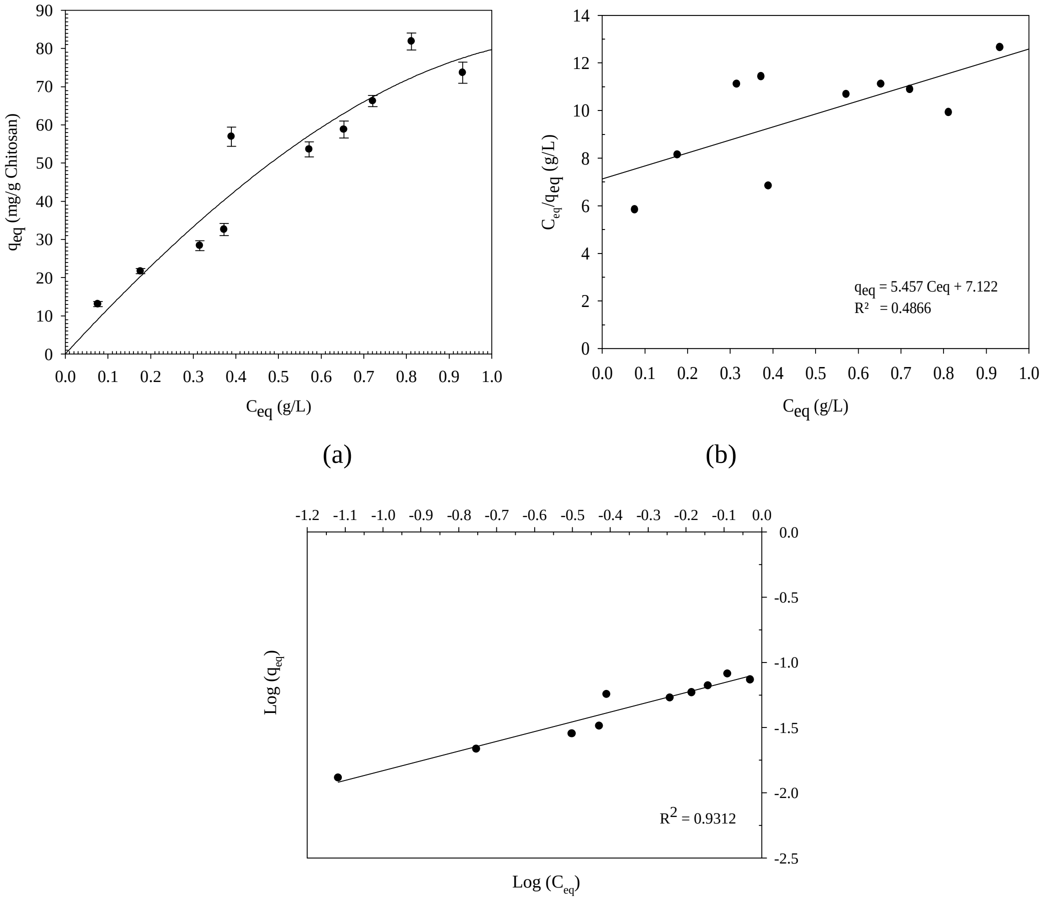


Figure 3: Variation of Chromium Uptake Capacities with Different Initial Cr Concentrations at 30 ^{0}C and 5.0 pH. Uptake Capacity Increases Non-Linearly with initial Cr Concentration

Equilibrium isotherm and its Langmuir and Freundlich depictions are given in Figure 4, and Langmuir and Freundlich's coefficients are given in Table 2.



(a) (b)

(c)

Figure 4 a) Equilibrium isotherm for Hexavalent Chromium
b) Lanmuir representation of isotherm
c) Freundlich representation of isotherm.
Freundlich plot gives a better fit for the acquired data

Table 2 - Langmuir and Freundlich constants for the model

Langmuir		Freundlich	
Q	b	Kf	n
0.183	0.767	0.339	1.336

As shown in Figure 4, Freundlich plot gives a better fit than Langmuir plot. Langmuir isotherm is based on the assumptions of monolayer adsorption and limited active sites, which means once an ion is attached to an active site, no further adsorption can take place at that site. Diversion of the experimental data points from Langmuir isotherm may be a result of this system not satisfying those two assumptions. The R^2 value for the Freundlich isotherm is 0.93, showing that the Freundlich equation can be effectively used to explain adsorption behavior.

The behavior of adsorption isotherm can be explained using the dimensionless separation factor $R_{L,}$ which is defined by

$$R_L = \frac{1}{1+bC_f}$$

For effective adsorption, R_L value have to be between 0 and 1. R_L values above 1 imply very weak attachment to the surface, which leads to reduced Chromium removal efficiency. On the contrary, R_L values which are very close to zero are the sign of irreversible attraction, which causes difficulties in the regeneration of the adsorbent (Ngah et al., 2006). R_L values obtained for each initial Cr (VI) concentration are given in Table 3, which shows that for initial Cr (VI) concentrations between 0.1-1 g/L, separation factor lies in the favorable range.

Table 3: Separation Factors at each Initial Ion Concentration

C_0 (g/L)	C_f (g/L)	R_L
0.1	0.076	0.945
0.2	0.176	0.881
0.3	0.315	0.805
0.4	0.372	0.778
0.5	0.390	0.770
0.6	0.572	0.695
0.7	0.653	0.666
0.8	0.721	0.644
0.9	0.812	0.616
1.0	0.932	0.583

The values of Q and K_F obtained in this experiment are somewhat lower than the values reported in the literature (Ngah et al., 2006; Sankararamakrishnan, Dixit, Iyengar, & Sanghi, 2006), which may have resulted from the lack of porosity in Chitosan particles. Low Q and K_f values imply difficulties in surface adsorption, which may be the reason for comparatively low Chromium removal percentage. Reducing the particle size further or using porous Chitosan beads are potential techniques to improve the adsorption of Chromium ions on the surface.

EFFECT OF PH

It can be seen in Figure 5 that the Chromium uptake capacity decreased with increasing pH throughout the selected range of 4 to 10. A rapid decrease in uptake capacity has been observed from pH 6 to 7, compared to the comparatively slow decrease from pH 4 to 6 and pH 7 to 10. These results suggest that chromium removal is most efficient at acidic pH, which agrees with previously reported work (Udaybhaskar et al., 1990). At acidic conditions, Cr (VI) exists as $Cr_2O_7^{2-}$ ions, and the amine groups in Chitosan are protonated, giving a positive charge to Chitosan particles. The strong interactions between positively charged Chitosan and negatively charged $Cr_2O_7^{2-}$ ions increases the uptake capacity of Chitosan at low pH values (Ngah et al., 2006; Sankararamakrishnan et al., 2006).

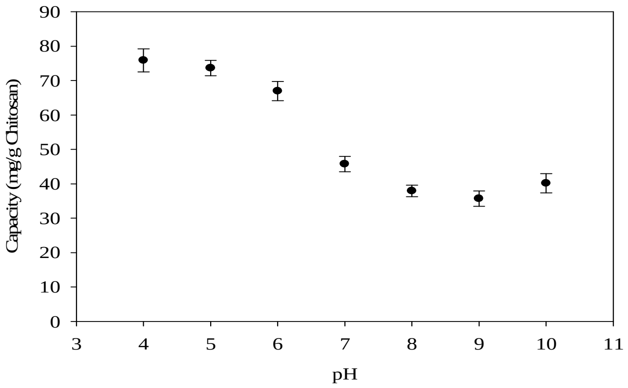


Figure 5: Variation of Chromium Uptake Capacity with pH. Uptake Capacity is Higher at Acidic pH, with a Great Reduction in Capacity from pH 6 to 7

Effect of Cl Ion Concentration

The effect of Cl ion concentration was analyzed by adding NaCl. In this experiment, Chromium concentration was fixed at 1 mg/ml.

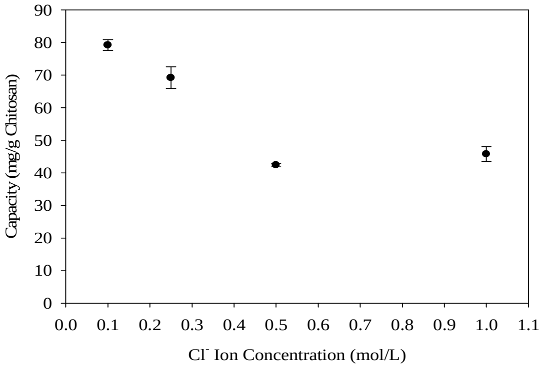


Figure 6: Variation of Chromium uptake Capacity with Cl- Ion Concentration. Uptake Capacity is Reduced at Higher Ion Concentrations

A decrease of chromium uptake capacity could be observed at increased ion concentrations, as shown in Figure 6. This can be attributed to the binding of Cl^- ions on the binding sites of chitosan. Attachment of negatively charged Cl^- ions to the positively charged amine groups in Chitosan will reduce the number of available sites for chromium adsorption, thus reducing chromium uptake capacity

CONCLUSIONS

Chitosan can be used as an effective adsorbent for removal of Hexavalent Chromium, especially at low Cr (VI) concentrations. Chromium adsorption capacity of Chitosan was determined to be 12 mg/g at 0.1 mg/ml Cr (VI) concentration and 51 mg/g at 1 mg/ml Cr (VI) concentration, which is higher than most of the reported natural adsorbents. While higher Cr (VI) concentrations lead to higher adsorption rates, the percentage removal of Cr (VI) becomes lower. Highest adsorption capacity is seen at acidic pH, with a drastic reduction between pH 5 and 6. While batch adsorption using Chitosan has given positive results, a comparison between batch and packed bed modes shows that continuously packed bed adsorption is the most efficient method to remove hexavalent Chromium from Chitosan.

REFERENCES

1. Arris, S., & Lehocine, M. B. (2014, 25-27 March 2014). *Removal of hexavalent chromium from industrial wastewater by Cereal By-Product.* Paper presented at the 2014 5th International Renewable Energy Congress (IREC).

2. Balasubramanian, S., & Pugalenthi, V. (1999). Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV–visible spectrophotometric methods. *Talanta, 50*(3), 457-467. doi:https://doi.org/10.1016/S0039-9140(99)00135-6

3. Baxter, A., Dillon, M., Anthony Taylor, K. D., & Roberts, G. A. F. (1992). Improved method for i.r. determination of the degree of N-acetylation of chitosan. *International Journal of Biological Macromolecules, 14*(3), 166-169. doi:https://doi.org/10.1016/S0141-8130(05)80007-8

4. Bhaumik, M., Setshedi, K., Maity, A., & Onyango, M. S. (2013). Chromium(VI) removal from water using fixed bed column of polypyrrole/Fe3O4 nanocomposite. *Separation and Purification Technology, 110*, 11-19. doi:https://doi.org/10.1016/j.seppur.2013.02.037

5. Chu, K. H., & Hashim, M. A. (2007). Copper biosorption on immobilized seaweed biomass: Column breakthrough characteristics. *Journal of Environmental Sciences, 19*(8), 928-932. doi:https://doi.org/10.1016/S1001-0742(07)60153-3

6. Dhungana, T., & Yadav, P. (2009). Determination of chromium in tannery effluent and study of adsorption of Cr (VI) on saw dust and charcoal from sugarcane bagasses. *Journal of Nepal Chemical Society, 23*, 93-101.

7. He, X., Li, K., Xing, R., Liu, S., Hu, L., & Li, P. (2016). The production of fully deacetylated chitosan by compression method. *The Egyptian Journal of Aquatic Research, 42*(1), 75-81.

8. Hexavalent Chromium. (2015). Retrieved from

   https://www.niehs.nih.gov/health/materials/hexavalent_chromium_508.pdf

9. Hu, J., Chen, G., & Lo, I. M. C. (2005). Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. *Water Research, 39*(18), 4528-4536. doi:https://doi.org/10.1016/j.watres.2005.05.051

10. Kotaś, J., & Stasicka, Z. (2000). Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution, 107*(3), 263-283. doi:https://doi.org/10.1016/S0269-7491(99)00168-2

11. Malkoc, E., Nuhoglu, Y., & Dundar, M. (2006). Adsorption of chromium(VI) on pomace—An olive oil industry waste: Batch and column studies. *Journal of Hazardous Materials, 138*(1), 142-151. doi:https://doi.org/10.1016/j.jhazmat.2006.05.051

12. Maruca, R., Suder, B. J., & Wightman, J. P. (1982). Interaction of heavy metals with chitin and chitosan. III. Chromium. *Journal of applied polymer science, 27*(12), 4827-4837. doi:10.1002/app.1982.070271227

13. N. P. Mendis, G. L. D. P. Gunawardana and S.H.P. Gunawardena. Possibility of using chitosan as an adsorbent in a continuous fixed-bed column for removal of hexavalent chromium. The 28th International Symposium on Transport Phenomena 22-24 September 2017, Peradeniya, Sri Lanka.

14. Ngah, W. S. W., Kamari, A., Fatinathan, S., & Ng, P. W. (2006). Adsorption of chromium from aqueous solution using chitosan beads. *Adsorption, 12*(4), 249-257. doi:10.1007/s10450-006-0501-0

15. Owlad, M., Aroua, M. K., Daud, W. A. W., & Baroutian, S. (2009). Removal of hexavalent chromium-contaminated water and wastewater: a review. *Water, Air, and Soil Pollution, 200*(1-4), 59-77.

16. Rhazi, M., Desbrières, J., Tolaimate, A., Rinaudo, M., Vottero, P., Alagui, A., & El Meray, M. (2002). Influence of the nature of the metal ions on the complexation with chitosan.: Application to the treatment of liquid waste. *European Polymer Journal, 38*(8), 1523-1530. doi:https://doi.org/10.1016/S0014-3057(02)00026-5

17. Sankararamakrishnan, N., Dixit, A., Iyengar, L., & Sanghi, R. (2006). Removal of hexavalent chromium using a novel cross linked xanthated chitosan. *Bioresource Technology, 97*(18), 2377-2382. doi:

    https://doi.org/10.1016/j.biortech.2005.10.024

18. Sarin, V., & Pant, K. K. (2006). Removal of chromium from industrial waste by using eucalyptus bark. *Bioresource Technology, 97*(1), 15-20.
19. Singh, P., & Nagendran, R. (2016). A comparative study of sorption of chromium (III) onto chitin and chitosan. *Applied Water Science*, *6*(2), 199-204. doi:10.1007/s13201-014-0218-2
20. Udaybhaskar, P., Iyengar, L., & Rao, A. V. S. P. (1990). Hexavalent chromium interaction with chitosan. *Journal of applied polymer science, 39*(3), 739-747. doi:10.1002/app.1990.070390322
21. Yuan, Y., Chesnutt, B. M., Haggard, W. O., & Bumgardner, J. D. (2011). Deacetylation of chitosan: material characterization and in vitro evaluation via albumin adsorption and pre-osteoblastic cell cultures. *Materials, 4*(8), 1399-1416.