ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Adsorption studies of Hexavalent Chromium using *Syzygium cumini* bark

A.Muthulakshmi*[1,2], R.Baskaran[3], N. Ashwin Karhik[4]
[1]Sathyabama University, Chennai, Tamil Nadu, India.
[2]Jeppiaar Engineering College, Chennai, Tamil Nadu, India
[3] Department of Chemical Engineering, St. Joseph's Engineering College, Chennai, Tamil Nadu, India.
[4]Centre of Nanoscience &Technology, AC College of Technology, Anna University, Chennai, Tamil Nadu, India.
***Corresponding Author: E-mail: visitmuthu1980@gmail.com; Mobile: 9942190046**

ABSTRACT

Heavy metal contamination has been implicating the health of people to a large extent. Of heavy metals, chromium is of high importance due to its toxicity. The site contaminated with chromium necessitates a potential remediating method for its removal. Adsorption of chromium has been widely studied and plant parts can be used as potential remediators. Hence, the objective of the present study is study the chromium adsorption properties of *Syzygium cumini* bark in aqueous solutions. The adsorption properties of the plant were studied under various conditions such as pH, contact time, initial metal ion concentration and adsorbent dosage. The maximum adsorption was observed at pH 4.0 with 1g of bark, onto which 46.82 mg of chromium in 2 hours. The adsorption of chromium was found to be stable and no desorption was found to occur at any pH. The optimization studies showed that increasing or decreasing of the adsorbate concentration decreased the amount of chromium adsorption. And also it was observed that the adsorption was linear and increased with time.

Keywords: *Syzygium cumini*, Chromium adsorption, Optimization of adsorption, stable adsorption.

1. INTRODUCTION

The concentration of chromium in the environment is increasing rapidly due to its use in leather, electroplating, steel, cement, pigments and refractories (Mishra et al., 2009). Chromium existing as Cr (VI) is known to cause ulcer, liver damage, pulmonary congestion and odema (Raji and Anirudhan, 1998). Also, Chromium has been termed as a potential carcinogen by the US EPA (2014). Hence, there exists a need to remediate the sites contaminated with chromium especially water bodies where the maximum chromium concentration has been limited to 100µg/l (Lalvani, 1998). For removal of chromium from aquatic bodies, various methods has been studied, of which, adsorption using has been promising (Gupta and Babu, 2006).

Activated carbon is the most widely used adsorbent and is reported to have high efficiency in the sorption of Cr (VI) (Bailey, 1999). However its use in industries is restricted mainly due to its high cost. Hence low cost natural adsorbents are of demand and are studied widely for the adsorption of metals. However, the lacuna is that these natural adsorbents are less efficient in adsorbing high concentrations of metal ions. Thus, there exists a need for a low cost natural material for adsorption of high concentrations of chromium. Our previous report indicated that the leaves of *Tamarindus indica* were able to adsorb upto 56% of 1000mg/l Chromium in 30 min with 4g/L adsorbent. However, the adsorption was not steady and desorption was found to occur with the course of time. Hence, a stable, high efficiency natural adsorbent is required for the adsorption of chromium.

The efficiency of *Syzygium cumini* bark is thus studied in the present study for adsorption of chromium. *S. cumini* is commonly called as Jamun or jambul and belongs to the family Myrtaceae. Adsorption of chromium using *Syzygium cumin* has been largely studied with the seeds (Singh et al., 2015; Sibichakkaravarthi and Vinitha Judith, 2015; Laxminarayana and Reddy, 2012) and bark (Singh et al., 2014). However, the efficiency of adsorption is very low.Hence, the study intends to evaluate the adsorption efficiency of *Syzygium cumini* bark at high concentrations of Chromium.

2. MATERIALS AND METHODS

Sample collection and preparation: The bark scrapings of *Syzygium cumini* were collected from Chennai, Tamil Nadu, India. The collected bark sample was washed and shade in room temperature for 6 days. The dried bark was powdered and sieved to obtain uniform size of 300µm. (ASTM-E11 No.50)

Preparation of effluent sample and optimization of adsorbate concentration: The collected effluent was analysed for concentration of chromium using DPC method (APHA, 2005) where it forms a purple coloured solution on reaction.The absorbance of the solution was read at 540 nm after 20 min. The effluent was then diluted to obtain an initial adsorbate concentration 1000mg/L) was appropriately diluted to form concentrations of 250, 500, 750 and 1000mg/L. 100ml of the effluent of varying adsorbate concentrations (250, 500, 750 and 1000mg/L) were taken separately in a 250ml conical flask containing 1g of the adsorbent samples. The mixture was stirred gently in a stirrer at 150rpm for 60min and allowed to settle for 10min. The solution was then filtered using Whatman filter paper and the concentrations of the metal ions in the filtrate were analysed by DPC method using UV spectrophotometer. The amount of chromium adsorbed was calculated using the following equation:

$q = (C0 - Ce)\ V/\ W$

where, q amount of Cr(VI) adsorbed by the adsorbent (mg/g),

C_0 is the initial concentration of Cr(VI) and Ce is the concentration of chromium at equilibrium (mg/ml),
V is the initial volume of chromium solution (ml),
And W is the weight of the adsorbent (g).

Optimization of pH, agitation time and adsorbent concentration: The effluent with desired adsorbate concentration was taken further for the optimization of pH, agitation time and adsorbent concentration. For this, 100ml of effluent was taken in conical flask and the pH was adjusted to 2, 3, 4, 5 and 6 with 1N HCl or 1N NaOH. Varying amounts of adsorbents such as 0.5, 1.0, 1.5 and 2 g were studied in each of the pH range. This reaction setup was prepared for agitated at 200rpm for different times such as 30, 60, 90 and 120min. After treatment at the above said conditions the metal ion concentration was estimated.

3. RESULTS AND DISCUSSIONS

The adsorption of chromium was initially performed with various concentrations of chromium, to optimize the concentration of chromium to be used for the study. Since, Cr (VI) released in the effluents is of high concentrations, ranging from 0.5 to 270, 000 (mg/L) and large volume (Patterson, 1985; Huang et al., 2009; Nriagu et al., 1988) an efficient method for removal of chromium from such water is required. The present study was conducted in real time effluents to study the efficiency of removal.

The results indicated that the adsorption increased linearly with concentration and hence, 1000mg/L was chosen as optimum concentration for the study as shown in Table 1. The evaluation of chromium was performed using 1, 5-diphenyl carbazide with UV-spectroscopy (APHA 2005), as not much difference was observed between the estimated chromium in this method to that estimated using Atomic absorption Spectroscopy. Using 1000 mg/L concentration of chromium, the experiment was carried out in batches of 200mL solutions. The adsorption of chromium was evaluated under various hydroxyl ion concentrations. The results indicated that the adsorption was enhanced when the hydroxyl ion concentration was increased from pH 2 to pH 4, beyond which there was a decrease in adsorption efficiency. The zero point of charge or the pH at which the chromium ions remain in equilibrium is pH 6.0 and below (Cotton and Wilkinson, 1980; Greenwood and Earnshaw, 1984; Swietlik, 1998; Darko et al., 2011) and hence the experiment was restricted to pH 2-6, as beyond this pH the chromium ions exist as hydroxides or chromate ions (Amarasinghe and Williams, 2007; Gebrehawaria et al., 2014). Adsorption is based on the exchange of ion species between the adsorbent and the adsorbate. Here the metal species (Cr (VI)) is positively charged below pH 6.0 and the surface of the bark powder is also protonated and exchange occurs between the surface of the adsorbent and the metallic salt (Yu et al., 2003).

The contact time plays a crucial role in adsorbing the metal species onto the surface of the adsorbent. The adsorption of chromium was studied in a time interval of 30 min upto 120 min under all hydroxyl ion concentrations. The results showed that the adsorption was rapid initially and obtained a mere equilibrium with time.The rapid adsorption of the chromium ions initially, is largely due to the large number of vacant sites present at the surface of the adsorbent initially (Wang et al., 2008; Mezenner, 2009) whereas these sites are occupied with time and thus slows the rate of adsorption (Owamah, 2014).

The present study indicates that the adsorbate dosage had role in the rate of adsorption, as it was observed that adsorbate dose of 1g showed maximum adsorption. The adsorption of chromium increased when the adsorbate dose was increased from 0.5 g to 1g for 150 ml solution of 1000mg/L chromium. However, beyond this there was a decrease in adsorption efficiency. The initial increase may be due to increase in surface area of the sorbent, thus making it probable that the chromium ions are adsorbed onto the adsorption sites, increasing the efficiency of adsorption (Nameni et al., 2008). However, beyond 1g of adsorbent, the efficiency of adsorption decreased similar to our previous study (Muthulakshmi et al., 2016) which may be largely due to crowding of adsorbent particles (Kumar and Kirthika, 2009).

The adsorption was found to be greater than previous reports using *Syzygium cumini*. The bark of *S. cumini* was reported to adsorb 31mg/L of chromium (Singh et al., 2014), however in the present study, the adsorption was 46mg/L of chromium. Figure 1 represents Percentage Adsorption of Cr (VI) by *S. cumini* bark with respect to various adsorbent mass and contact times at different pH.

Table.1.Percentage Adsorption of Cr (VI) by *S. cumini* bark with respect to various adsorbent mass and contact times at different pH

Adsorbent concentration (per 100 mL)/ Time		30 min	60 min	90 min	120 min
pH 2.0	0.5g	1.43	8.91	11.38	17.62
	1g	15.05	22.38	29.71	33.37
	1.5g	1.33	10.49	19.64	24.22
	2g	3.67	5.18	6.69	12.44
pH 3.0	0.5g	9.75	16.45	23.15	26.50

	1g	31.35	35.17	38.99	40.90
	1.5g	20.58	25.79	31.05	33.68
	2g	18.38	23.93	29.48	32.25
pH 4.0	0.5g	13.29	19.52	25.74	28.86
	1g	40.23	42.87	45.51	46.82
	1.5g	29.71	33.74	37.78	39.80
	2g	21.42	26.57	31.71	34.28
pH 5.0	0.5g	10.84	17.40	23.95	27.23
	1g	29.56	33.61	37.67	39.70
	1.5g	24.72	29.42	34.12	36.48
	2g	10.43	17.05	23.66	26.96
pH 6.0	0.5g	2.37	12.05	15.74	21.58
	1g	13.68	22.52	31.36	35.78
	1.5g	13.01	20.61	28.21	32.01
	2g	3.71	11.28	21.85	27.13

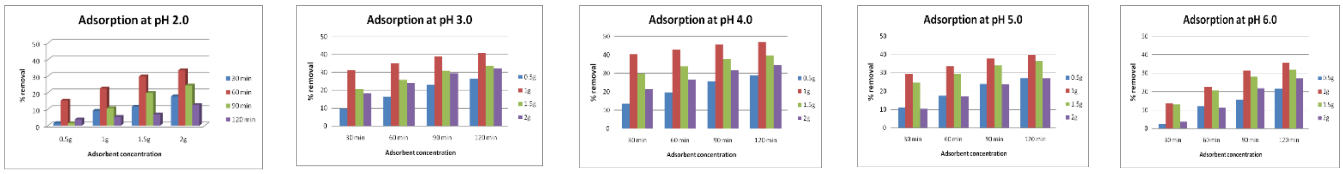

Figure.1.Percentage Adsorption of Cr (VI) by *S. cumini* bark with respect to various adsorbent mass and contact times at different pH

4. CONCLUSION

The present study investigates the adsorption of Chromium by bark of *Syzygium cumini*. The effluent was diluted to obtain 250, 500, 750 and 1000 mg/L concentration of chromium. It was observed that the adsorption percentage increased with concentration and hence 1000 mg/L was chosen as optimum concentration for further studies. The effect of pH and adsorbent concentration on adsorption of chromium was evaluated. The results showed that maximum adsorption was at pH 4.0 with adsorbent concentration 1g/100 mL. The adsorption was found to increase with time and at 2 h, maximum adsorption of 46% was reached during the time interval studied. The maximum adsorption of 46mg/g of adsorbent is a considerable rate, and activation of the sample may yield higher adsorption capacity.

REFERENCES

Amarasinghe BMWPK, Williams RA, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chem. Eng. J, 132, 2007, 299–309.

APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association/American Water Works Association/Water Environment Federation, 2005, USA.

Bailey SE, Olin TJ, Brick RM, Adrian DD, A review of potentially low-cost sorbents for heavy metals. Water Research, 33, 1999, 2469-2479.

Cotton FA, Wilkinson G, Chromium. In: Advanced inorganic chemistry: a comprehensive text, 4th edn. Wiley, New York, 1980, 719–736.

Darko HA, Tatjana DA, Ruzica SN, Milovan MP, Srdjan DB, Aleksandar LB, Milica MR, Leaching of chromium from chromium contaminated soil: a speciation study and geochemical modeling. J Serb. Chem. Soc, 76, 2011, 1–20.

Gebrehawaria G, Hussen A, Rao VM, Removal of hexavalent chromium from aqueous solutions using barks of *Acacia albida* and leaves of *Euclea schimperi.* Int. J. Environ. Sci. Technol, 2014, DOI 10.1007/s13762-014-0530-2.

Greenwood NN, Earnshaw A, Chemistry of the elements. Pergamon Press, Oxford, 1984, 1187–1200.

Gupta S, Babu BV, Adsorption of chromium (VI) by a low-cost adsorbent prepared from tamarind seeds. In: Proceedings of International Symposium & 59th Annual Session of IIChE in association with International Partners (CHEMCON-2006), GNFC Complex, Bharuch, 2006, December 27–30.

Kumar PS, Kirthika K, Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto Bael tree leaf powder. J Eng. Sci. Technol, 4(4), 2009, 351–36.

Laxminarayana K, Reddy KL, Removal of Cr(VI) Ions from Aqueous Solution by Using *Syzygium cumini* Seeds. Asian Journal of Chemistry, 24(12), 2012, 5771.

Lalvani SB, Wiltowski T, Hubner A, Weston A, Mandich N, Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent. Carbon, 36, 1998, 1219–1226.

Mezenner YN, Bensmaili A, Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. Chem. Eng. J, 147, 2009, 87–96.

Mishra K, Gupta K, Rai UN, Bioconcentration and phytotoxicity of chromium in *Eichhornia crassipes*. J. Environ. Biol, 30(4), 2009, 521-26.

Muthulakshmi A, Baskaran R, Ashwin karthick N, Removal of Chromium from Aqueous Solution Using *Tamarindus indica* Leaves as Adsorbent. Journal of Environmental Biology, 2016 (Accepted).

Nameni M, Moghadam MRA Arami M, Adsorption of hexavalent chromium from aqueous solutions by wheat bran. Int. J. Environ. Sci. Tech, 5, 2008, 161–168.

Nriagu JO, Pacyna JM, Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333, 1988, 134−139.

Owamah HI, Biosorptive removal of Pb(II) and Cu(II) from waste water using activated carbon from cassava peels. J. Mater. Cycles. Waste. Manag, 16, 2014, 347–358.

Patterson JW, Industrial Wastewater Treatment Technology, second ed., Butterworth-Heinemann, 1985, London.

Raji C, Anirudhan TS, Batch Cr (VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics. Water Research, 32(12), 1998, 3772-3780.

Sibichakkaravarthi LM, Vinitha Judith, Removal of hexavalent chromium from wastewater using *Syzygium cumini* seed as an adsorbent. International Journal for Technological Research in Engineering, 2(9), 2015, 2347 - 4718.

Singh S, Tripathi A, Srivastava SK, Removal of hexavalent chromium from contaminated waters using *Syzygium cumini* seed biosorbent. International Journal of Engineering Research and General Science, 3(3), 2015 429-438.

Singh S, Tripathi A, Srivastava SK, Prakash R, Biosorption efficiency of *Syzygium cumini* (L.) bark for removal of hexavalent chromium from contaminated waters. Poll Res, 33 (2), 2014, 271-279.

Swietlik R, Speciation analysis of chromium in waters. Pol. J. Environ. Stud, 7 (5), 1998, 257-266.

US EPA: Priority Pollutant List, 40 CFR Part 423, Appendix A, 2014.

Wang S, Jin X, Zhao H, Wu F, Phosphate biosorption characteristics of a submerged macrophyte *Hydrilla verticillata*. Aquat. Bot, 89(1), 2008, 23–26.

Yu LJ, Shukla SS, Dorris KL, Shukla A, Margrave JL, Adsorption of chromium from aqueous solution by maple saw dust. J. Hazard. Mater, 100, 2003, 53 – 63.