

Adsorption Efficiency of Hexavalent Chromium Ions From Synthetic Wastewater Using Simple Ascidian *Ascidia Sydneiensis*

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Abstract- Heavy metals are well-known for their persistent biodegradation and accumulation in living organisms causing serious health problems. The efficient removal of heavy metals from synthetic waste water is among the most essential issues for a lot of industrialized countries. The chemically activated adsorbent prepared from simple ascidian *Ascidia sydneyensis* was used to remove Chromium (VI) from synthetic waste water in batch studies by adsorption process. Parameters such as pH, adsorbent dose, contact time between solution and adsorbent were evaluated. The binding capacity of activated adsorbent of this species was estimated using electrochemical methods such as Cyclic Voltammetry (CV), Differential Pulse Voltammetry and Square Wave Voltammetry (SWV) before and after adsorption with Chromium (VI). The results revealed that the effective adsorption of Chromium (VI) was within the range of 92.4 % using activated carbon of *Ascidia sydneyensis*. Based on the studies, the activated adsorbent prepared from marine ascidian *Ascidia sydneyensis* holds a vast potential in the removal of heavy metals from synthetic waste water.

Index Terms- Adsorbent; *Ascidia sydneyensis*; Batch studies; Electrochemical methods.

1. INTRODUCTION

Water is the important ingredient of animal and plant life. It acts as a solvent for the secretory and excretory products in human body. Water performs as a carrier of nutritive elements to tissues and removes waste materials from them [1]. Heavy metal pollution has become a major issue in many countries because their existence in drinking and wastewaters often exceed the permissible standards [2]. In India, drinking water is contaminated at many places by various pollutants [3]. The effluents from metallurgical industries and mining sectors contain heavy metal ions which are toxic to the living organisms. Chromium is a highly toxic metal and its presence in hexavalent form is one of the most environmental problems due to the human health associated risk [4]. The maximum permissible level of Chromium (VI) in drinking water is 0.05 mg/L and the tolerance limit for Chromium (VI) to discharge into land surface waters is 0.1, 2, 5 and 7 mg/L. Because of its high toxicity, Chromium (VI) must be substantially removed from the wastewater before being discharged into the aquatic system [5].

Biosorption has emerged as a cost-effective and efficient alternative treatment technology for removal of heavy metals [6]. This involves the inter-phase accumulation of concentration of substances at a surface or at the inter-phase [7]. Activated adsorbent is

the most widely used adsorbent but commercially available activated adsorbent are very expensive [8]. Different types of biocarbon in non-living form have been studied for their heavy metal uptake capacities. Bacteria, fungi, algae, plant leaves and root tissues were used as biosorbents for recovery of metals from industrial discharges [6]. In this study an attempt was made to determine the effectiveness of the activated biocarbon derived from a simple ascidian *Ascidia sydneyensis*. This species belongs to family Ascidiidae and commonly available in Tuticorin harbor. Early investigations on chemical studies [9-12], toxicity [13], anti-diabetic [14], hepatoprotective [15], anti-hyperlipidemic [16], cardioprotective [17] and anti-fertility [18] activities of *Ascidia sydneyensis* have already been recorded. Since no report on adsorption efficiency is available, the present work was attempted. This species was used to remove chromium (VI) from wastewater and to investigate the mechanisms of adsorption onto activated carbon by performing a batch experimental process. The present investigation was aimed to study the effects of adsorbent dosage, contact time and pH for the removal of Chromium (VI) ions from wastewater using the activated carbon. The metal biomass interaction responsible for biosorption with untreated and metal treated biomass was confirmed by electrochemical studies of activated carbon of *Ascidia sydneyensis* powder.

2. MATERIALS AND METHODS

2.1. Collection of animal material

Samples of *Ascidia sydneiensis* were collected from Tuticorin coast and identified using key to identification of Indian ascidians [19,20]. A voucher specimen AS 2252 has been deposited in the National Collections of Ascidians in the Museum of the Department of Zoology, A.P.C. Mahalaxmi College for Women, Tuticorin-628002.

2.2. Processing

Epibionts adhering to the test were carefully removed, washed with sterile sea water, dried under shade and homogenized to get a coarse powder, which was stored in an air tight container and used for further investigations. The dried animal material was granulated or powdered by using a blender. The powder was sieved to get uniform particles by using sieve No. 60. The final uniform powder was used for the adsorption studies.

2.3. Preparation of activated carbon

One part by weight of *Ascidia sydneiensis* was treated with concentrated sulphuric acid. It was kept at 150 °C in an air oven for one day. The carbonized material was cleaned well with water to remove free acid. It was dried at 100 - 105 °C for 24 hrs. The adsorbent was ground, sieved and packed in airtight containers.

2.4. Preparation and analysis of adsorbate

A chromium stock solution of desired strength was prepared by dissolving calculated weight of potassium dichromate in distilled water. Chromium (VI) metal elements were measured by using photocolorimetric methods as per the following procedures (Manual of methods of analysis of foods, food safety and standard authority of India) [21]. The development of a purple - violet colour with 1,5 diphenyl carbazide in acidic solution as complexing agent. The absorbance of this solution was read at 540 nm.

2.5. Batch adsorption experiments

To evaluate the effect of the biosorbent in Chromium (VI) removal from waste water batchwise shaking of conning bottle experiments were performed by using mechanical shaker at room temperature. The experiments were conducted with various adsorbent dose (10 - 100 mg / 25 mL), in continuously shaken conning bottles having 25 mL of synthetic effluent Chromium (VI) metal ions with contact time ranging from 10-60 minutes and at pH values varying from 0.5 - 10.5. The shaken samples were then filtered and

the strength of chromium (VI) ions in the filtrates analyzed colorimetrically.

The percentage removal and uptake capacity of chromium (VI) by activated carbon of *Ascidia sydneiensis* was calculated using the equation.

$$\% \text{ Removal} = (C_{\text{initial}} - C_{\text{final}}) \times 100 / C_{\text{initial}}$$

C_{initial} - initial concentration of Chromium (VI) without sample.

C_{final} - final concentration of the filtrates after treatment.

2.6. Electrochemical Methods

Cyclic Voltammetry (CV), Differential Pulse Voltammetry and Square Wave Voltammetry (SWV) are performed with a CHI 650C electrochemical workstation. The working electrode is a glassy carbon electrode (GC). An Ag/AgCl electrode and platinum wire are used as the reference electrode and counter electrode. At room temperature, all electrochemical experiments are carried out in a single compartment electrochemical cell.

2.6.1. Cyclic voltammetry

Cyclic Voltammetry is the most widely used electrochemical technique acquiring qualitative information about electrochemical reactions. Cyclic voltammograms trace the shift of electrons during redox reaction. The potential of an electrode in solution is linearly cycled from a starting potential to final potential and back to the starting potential. Here, the current is measured as a function of potential. This process, in turn, cycles the redox reaction. Single or multiple cycles can be applied. The system starts off with an initial potential at which no redox can take place.

2.6.2. Differential Pulse Voltammetry

In Differential Pulse Voltammetry, the base potential is incremented from Initial E toward Final E. A potential pulse is applied. The current before the potential pulse and at the end of the potential pulse are sampled. The difference of these two current samples is recorded as the function of potential. The potential waveform applied as the function of time and the current sampling scheme.

2.6.3. Square Wave Voltammetry

In Square Wave Voltammetry, the base potential is increased from Initial E towards Final E. A square

wave potential is superimposed to the base potential. The base potential increased after each cycles of the square wave. The current at the end of forward and reverse steps are sampled. These two currents are observed as the function of the base potential. The potential waveform applied as the function of time.

3. RESULTS AND DISCUSSION

3.1. Effect of adsorbent dosage

From the study the dosage variation of *Ascidia sydneiensis* adsorbent it was seen that adsorption of chromium (VI) onto the sorbents increases with increase in adsorbent dosage from 10 - 100 mg (Figure 1).

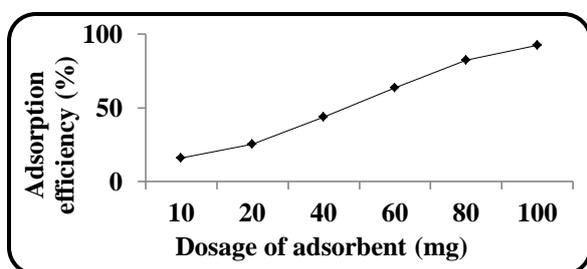


Figure 1. Adsorption efficiency of chromium (VI) - adsorbent dosage.

The maximum adsorption of chromium (VI) was found to be 92.4 % on *Ascidia sydneiensis* adsorbent is obtained in Table 1.

Table 1. Adsorption efficiency of Chromium (VI) - adsorbent dosage.

Dosage of adsorbent (mg)	Adsorption Efficiency (%)
10	16.1
20	25.2
40	43.6
60	63.4
80	82.3
100	92.4

Maximum adsorption occurs at about 100 mg adsorbent dosage whereas further increase thereafter in the quantity of the adsorbent has no more effect to the adsorption rate. Therefore the study indicated that 100 mg of adsorbent is sufficient to adsorb the maximum ions.

3.2. Effect of contact time

The efficiency of adsorption was found to increase with increase in contact time (10-60 minutes). The maximum adsorption efficiency of Chromium (VI) was found to be 90.6 % on *Ascidia sydneiensis*

adsorbent at pH 2.5 with 100 mg of adsorbent was shown in Table 2 and Figure 2.

Table 2. Adsorption efficiency of Chromium (VI) - contact time variation.

Contact Time (minutes)	Adsorption Efficiency (%)
10	24.3
20	41.5
30	56.8
40	62.4
50	78.2
60	90.6

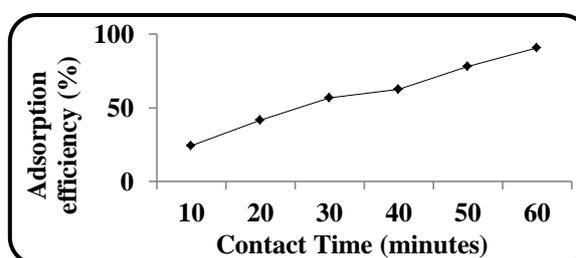


Figure 2. Adsorption efficiency of chromium (VI) - contact time variation.

The maximum adsorption occurs at contact time 60 minutes.

3.3. Effect of pH variation on the adsorption of chromium (VI)

The results of pH variation show that the process of adsorption is highly pH dependent. The maximum adsorption of Chromium (VI) was found to be 86.3 % on *Ascidia sydneiensis* adsorbent at pH 2.5 with 100 mg of adsorbent were reported in Table 3 and Figure 3.

Table 3. Adsorption efficiency of Chromium (VI) - pH variation.

pH	Adsorption Efficiency (%)
0.5	70.8
2.5	86.3
4.5	55.3
6.5	46.4
8.5	17.6
10.5	5.5

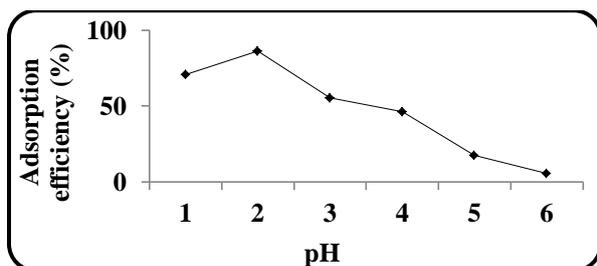


Figure 3. Adsorption efficiency of chromium (VI) - pH variation.

The maximum adsorption occurs at suitable pH of 2.5. The pH of solution was examined at different pH levels, covering a range of 0.5 - 10.5. In the case of Chromium (VI) the maximum adsorption was obtained at pH of 2.5 for dosage adsorbent (100 mg in 250 µg/L).

3.4. Electrochemical Techniques - Removal of Chromium (VI) before and after adsorption with *Ascidia sydneiensis* adsorbent

3.4.1. Cyclic voltammetry

An activated carbon of *Ascidia sydneiensis* before and after adsorption with chromium (VI) solution was carried out using cyclic voltammogram. At an optimized pH 1.0, cyclic voltammogram of chromium (VI) solution was studied on GCE. Chromium (VI) solution without biosorbent treatment exhibited one oxidation and reduction peaks at + 0.05 V and -0.5 V. Chromium (VI) adsorbed by *Ascidia sydneiensis* showed lesser oxidation peak at + 0.1 V. It was represented in Figure 4.

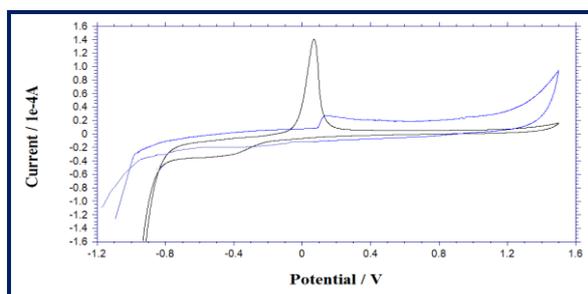


Figure 4. Cyclic voltammogram for Chromium (VI) after and before treatment.

This is because of good adsorption efficiency of *Ascidia sydneiensis*. The background current was noted for all scan rates investigated in the potential range from - 0.2 to 1.6 V.

3.4.2. Differential pulse voltammetry

Before and after adsorption of *Ascidia sydneiensis* with chromium (VI) solution was studied using differential pulse voltammogram. Chromium (VI) solution was carried out at pH 1.0 on GCE for differential pulse voltammogram. It was scanned in the forward direction. Chromium (VI) solution indicated one anodic peak in the forward scan. *Ascidia sydneiensis* after adsorption treatment with chromium (VI) solution indicated lesser anodic peak at -0.8 V. It was observed in Figure 5.

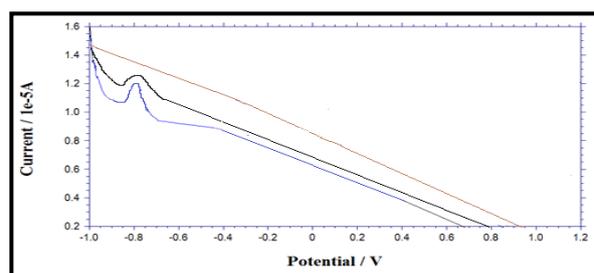


Figure 5. Differential pulse voltammogram for chromium (VI) after and before treatment.

This is because of excellent behaviour of adsorption capacity of *Ascidia sydneiensis*. The background current was recorded for all scan rates studied in the potential range from - 1.0 to + 0.1 V.

3.4.3. Square wave voltammetry

An activated carbon of *Ascidia sydneiensis* before and after adsorption with chromium (VI) solution was determined using square wave voltammogram. At an optimized pH 1.0, square wave voltammogram of chromium (VI) solution was carried out on GCE. Square wave voltammogram of chromium (VI) solution without biosorbent exhibited one anodic peak. *Ascidia sydneiensis* after adsorption with chromium (VI) solution indicated lesser anodic peak at -0.02 V. It was shown in Figure 6.

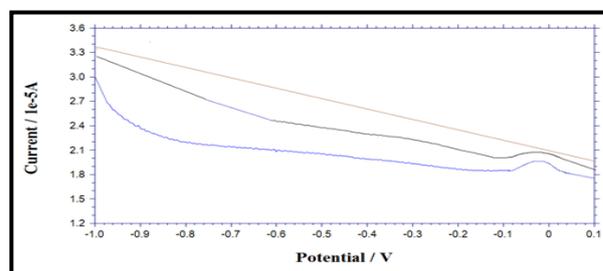


Figure 6. Square Wave Voltammogram for chromium (VI) after and before treatment.

This is due to the effective adsorption efficiency of *Ascidia sydneiensis*. The background current was recorded for all scan rates studied in the potential range from - 1.0 to + 1.2 V.

4. CONCLUSION

In current years, increasing prices and ecological considerations issued the use of innovative low or no cost activated carbons. The present investigation suggested that *Ascidia sydneiensis* can be applied as an efficient adsorbent for the removal of hexavalent chromium ions. The findings indicated that the enhancing adsorbent dose and contact time increases the removal capacity of Chromium (VI). The maximum adsorption was obtained at optimum pH of 2.5. Though the simple ascidian of *Ascidia sydneiensis* utilized for medicinal purpose can also be used as a good adsorbent for the removal of the toxic hexavalent chromium ions from wastewater.

REFERENCES

- [1] Sharma, B.K. (2001): Instrumental chemistry. Twelfth revised and enlarged edition (I), pp. 152.
- [2] El Hassouni, H.; Abdellaoui, D.; EL Hani, S.; Bengueddour, R. (2014): Biosorption of cadmium (II) and copper (II) from aqueous solution using red alga (*Osmundea pinnatifida*) biomass. Journal of Materials and Environmental Science, **5** (4), pp. 967 - 974.
- [3] Sadasivan, P.; Harikumar, P.; Jaseela, C.; Tharayil Megha, T. (2012): Defluoridation of water using biosorbents. Natural Science, **4** (4), pp. 245 - 251.
- [4] Belattmania, Z.; El Atouani, S.; Kaidi, S.; Bentiss, F.; Tahiri, S.; Reani, A.; Sabour I. (2018): Protonated biomass of the brown seaweed *Cystoseira tamariscifolia*: A Potential Biosorbent for Toxic Chromium Ions Removal. Research Journal of Environmental Sciences, **12**, pp. 106 - 113.
- [5] Miretzky, P; Cirelli, A.F. (2010): Chromium (VI) and chromium (III) removal from aqueous solution by modified lingo cellulosic materials. Journal of Hazard Materials, **180**, pp. 1-19.
- [6] Tamilselvan, N.; Saurav, K.; Kannabiran, K. (2011): Biosorption of selected toxic heavy metals using algal Species *Acanthopora spicifera*, Pharmacology Online, **1**, pp. 518 - 528.
- [7] Tien, C. (1994): Adsorption, calculations and modeling. Butter worth - Heinemann, USA, pp. 25.
- [8] Khare, S. K.; Pandey, K. K.; Srivastava, R. M.; Singh, V. N. (1987): Removal of basic dye (crystal violet) from water using wollastonite as adsorbent. Journal of Chemical Technology and Biotechnology, **38**, pp. 99.
- [9] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2013): Infra red and gas chromatogram - mass spectral studies of the ethanol extract of *Ascidia sydneiensis*. International Research Journal of Pharmaceutical and Applied Sciences, **3** (5), pp. 271 - 277.
- [10] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2015): Spectrophotometric studies of a simple ascidian *Ascidia sydneiensis*. Acta Chimica Pharmaceutica Indica, **5** (2), pp. 68 - 72.
- [11] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2013): Studies on the chemical constituents of a simple ascidian, *Ascidia sydneiensis*. In the proceedings of second International Conference of Kanniyakumari Academy of Arts and Science, pp. 32 - 35.
- [12] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2017): Heavy metal detection of a simple ascidian, *Ascidia sydneiensis* by using atomic absorption spectroscopy. In the proceedings of International Seminar of Multidisciplinary Research in Chemistry, pp. 48 - 51.
- [13] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2016): Evaluation of safety profile of *Ascidia sydneiensis* to wistar albino rats. World Journal of Pharmacy and Pharmaceutical Sciences, **5** (4), pp. 1740-1748.
- [14] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2016): Hypoglycemic potential of *Ascidia sydneiensis* Stimpson, 1855 on alloxan induced diabetic rats. International Journal of Science and Research, **5** (7), pp. 470 - 476.
- [15] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2016): Protective effect of against carbon tetrachloride induced hepatic injury. International Journal of Chemical and Pharmaceutical Analysis, **3** (4), 1-9.
- [16] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2017): Potential of against triton induced hyperlipidemia. European Journal of Pharmaceutical and Medical Research, **4** (1), 356 - 374.
- [17] Packiam, C.S.; Margret, R.; Meenakshi, V.K. (2017): Protective role of *Ascidia sydneiensis* Stimpson, 1855 on cardiac enzyme biochemistry and histopathology in isoproterenol - induced myocardial ischemia. International Journal of Pharmaceutical Chemistry, **7** (1), pp. 11 - 19.
- [18] Packiam, C.S.; Margret, R.J.; Meenakshi, V.K. (2016): *Ascidia sydneiensis*, Stimpson 1855 - a potent antifertility agent. International Journal of Research and Development in Technology, **6** (1), pp. 70 - 82.
- [19] Meenakshi, V. K. (1997): Biology of a few chosen ascidians. Ph.D., Thesis, Manonmaniam Sundaranar University, Tirunelveli, Tamilnadu, pp. 157-217.
- [20] Meenakshi, V. K.; Renganathan, T. K. (1997): On the occurrence of a simple ascidian *Ascidia sydneiensis* Stimpson, 1855 from Tuticorin coast of India. Geobios new Reports, **17**, pp. 71-72.
- [21] Manual of methods of analysis of foods, food safety and standard authority of India. (2012): Ministry of health and family welfare. Government of India, Newdelhi.