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STUDY ON THE EFFICACY OF THE *SARGASSUM WIGHTII* BIOCHAR ON THE REMEDIATION OF PARTIALLY TREATED TANNERY EFFLUENT OF RANIPET INDUSTRIAL AREA, INDIA

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Abstract
The current research investigated the ability of biochar of the marine macroalgae *Sargassum wightii* in the removal of Cr(VI) and the depletion of various physicochemical parameters including BOD, COD, TDS, TSS, TS, TH, turbidity, and electrical conductivity from the partially treated tannery effluents. The production of biochar was carried out at 300-600°C using a pyrolysis process and the highest carbon content was achieved at 600°C. The batch studies were conducted using algal biochar on the adsorption process at 30°C to examine the effects of pH, adsorbent dose, residence time, initial metal ion concentration, and desorption process. The maximum adsorption for the adsorbent was observed at pH 7, dosage of 6 gm/L, residence time of 6 hours, and initial metal concentration at 50 mg/L. The adsorption isotherms such as Langmuir and Freundlich models were employed and a better fit was observed in Freundlich with a high correlation. The pseudo-second-order kinetics was suitable (R>0.99) rather than pseudo-first-order kinetics. Based on the results, it is proved that the biochar with high carbon content was an excellent biosorbent in the remediation of tannery effluent.

Keywords: *Sargassum wightii* biomass, biochar, Tannery effluent, Treatment

Introduction

Our Indian economy largely depends on the leather industry as its turnover is nearly 2 billion US dollars in leather exports. It aims to improve the utilization of resources and environmentally friendly practices on a broad scale, focusing specifically on the manufacturing system's optimization by novel technology development (**Kumar et al 2012).** The Leather manufacturing companies need plenty of water and chemicals for their production. During the manufacturing processes, it releases a huge amount of effluents from the tannery industry. Among many toxic heavy metals, Cr(VI)is considered a toxic substance and it is one of the most common heavy metals which has been widely used and released by the industries. The maximum permissible level of Cr (VI) in an effluent discharge is 0.05 mg/L.

Vellore City is India's leading exporter of finished leather products, accounting for approximately 37% of the country's total leather exports (Thiripurasundari and Ponsakthisurya, 2018). For more than one decade, tanneries were running without and partially unregulated pollutant control. The environmental impact of tannery effluents has grown in recent years since they are the major source of pollution in aquatic systems (Yusif et al., 2016).

As an industrial hub, Ranipet is located around 120 miles south of Chennai. Inspite of the 2008 Global Financial Crisis, Ranipet, Tamilnadu, India was one of the major Exporters of foreign exchange in India, with annual exports estimated at about 240 million euros in 2012 (CLE. 2013; Kamala Marius and Govindan Venkatasubramanian., 2018). The Central Pollution Control Board of India has designated the Ranipet region as a chronically contaminated area. It is one of India's largest exporting centers for tanned leather. There are 240 tanneries in and around Ranipet town, as well as various chemical enterprises. A high average concentration of all contaminants was observed in the water at this location, with heavy metals like Chromium (average of 247.2 μg/L) and Copper (average of 95.5 μg/L).
Tannery effluents are identified by their strong colour, odour, acidity, and alkalinity (Essays 2018). Vijayakumar et al., (2022) have given the current status of the groundwater samples of Ranipet which is present around the tannery industrial areas. The research study shows a variation from 0.012 to 40.5 mg/L of Chromium (VI). The World Health Organisation states that the acceptable level of Cr (VI) in drinking water is 0.05 mg/L; any concentration above 0.1 mg/L can have detrimental effects on human health, including lung cancer, skin allergies, stomach, kidney, and liver damage (WHO, 2017). Based on the guidelines, it shows the amount of Cr^{6+} present is higher than allowed. This indicates that the anthropogenic causes of the elevated Cr6+ content are the chromium-based industries, tanneries, and incorrect waste disposal practices of these companies. When tannery effluents are released into open space, pollutants infiltrate and leach into the groundwater over time, which raises the chromium content.
The removal of Cr(VI) from the wastewater has been carried out by various processes. Among all, using adsorbent in the removal procedure is considered an effective and cheap method. Trikkaliotis *et al*.,(2022), reported that the adsorption procedure has been concentrated on removing toxic heavy metal ions, in order to provide a novel treatment method that avoids high cost and very risky procedures.
In recent years, there has been an increasing focus on using naturally available and cost-effective biomaterials to remove heavy metal ions from wastewater. This has led to the need for more efficient and affordable wastewater treatment methods to replace conventional ones (Masood et al., 2021).
Many researchers have identified various adsorbents for eliminating Cr(VI) using sources such as bacteria, fungi, and micro and macroalgae (Wang and Chen, 2009). According to the literature search, marine macroalgae *Sargassum wightii,* a brown alga is recognized as a potential adsorbent for heavy metal removal because its cell walls are largely made of various elemental groups such as carboxyl, hydroxyl, polysaccharides, chitin, and alginates, which have a remarkable binding affinity towards toxic pollutants from the tannery effluents (Benaisa *et al*.,2018; Khan et al., 2021)). With its rapid growth rates, brown algae can also be used to make biochar, which is another possible use for their biomass.

Recently, there has been a noticeable increase in interest in making biochar from algal biomass. Biochar is also known as charcoal which is rich in carbon content, a highly stable material, with high nutrient value, and ion exchange capacity. Due to its nature, algal biochar can be utilized as an adsorbent to remove organic as well as inorganic pollutants from wastewater. The conventional method used for the production of biochar is slow pyrolysis, in oxygen-limited circumstances where a thermal decomposition takes place between 350-650ºC (Chang et al., 2015). Pyrolysis is one of the most effective methods for transforming biomass into biochar.

The objective of this work is to use the biochar from algal biomass for the treatment of partially treated Tannery Industry effluent collected from CETP, Ranipet, Tamilnadu, India, and analyze the reduction of various physicochemical parameters and the heavy metal Chromium.

Materials and methods

Sampling

The sample was collected from a Common Effluent Treatment Plant (CETP), Ranipet, Ranipet district. For the current research work, we collected the effluent in plastic containers from the primary treatment tank. All of the samples were examined using conventional techniques for evaluating wastewater (APHA 1995).,

Potassium dichromate, sodium hydroxide, hydrochloric acid, sulfuric acid, phosphoric acid, sodium chloride, sodium sulphate, sodium nitrate, sodium bicarbonate, disodium phosphate, acetone, and additional chemicals were among the reagents. Analytically pure chemicals and reagents have been used for all the experiments. Deionized water was utilised in the preparation of each solution.

Preparation of biosorbent

In this current sorption experiment, *Sargassum whitti*, one of the brown marine algae considered as a potential biosorbent, and collected from the Bay of Mannar, Tamil Nadu, India. The first step was the repeated washing of the collected algae using deionized water to eliminate the undesirable components from it. The cleaned biomass was dried absolutely by exposure to sunlight for nearly 20 days. The scorched biomass is then sliced into smaller parts and converted into powder by a household blender.

Preparation of biochar

Biochar has been produced using a process called pyrolysis, which includes heating the biomass to a temperature of between 300 and 600 ºC to undergo a thermochemical breakdown. 10 gm of dried biomass from *Sargassum wightti* was weighed and taken in a muffle furnace with limited oxygen, this procedure was carried out gradually for an hour at a constant flow of N2.

Physicochemical study of the tannery effluent

Total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), chemical and biochemical oxygen demand (BOD and COD), total hardness, salinity, turbidity, electrical conductivity, and the presence of the heavy metal chromium were all determined for the samples that had been so collected. The APHA (1995) protocols and techniques have been employed for the estimation and analysis of physicochemical properties, and atomic absorption spectroscopy (Make: Shimadzu AA-7000) is used for quantifying heavy metals.

Adsorption Experiments by Batch Method

100 milliliters of tannery wastewater have been placed in 250 ml conical flasks for the batch adsorption experiments using 1 g of dried, powdered biomass/ biochar adsorbents. At room temperature, the flasks were shaken in an orbit shaker. By changing the pH of the solution from 2 to 8 for one hour of contact time, at a sorbent dosage of 1 g/100 ml, the effect of the initial pH level was investigated. 0.1 N HCl or 0.1 N NaOH were used to change the pH of wastewater. In the range of 1-6 hours and 1-6 grams, the impact of the contact period and the amount of adsorbent on the sorption capacity of sorbent was investigated. After that period of time, the solution was filtered using Whatman filter paper No. 42, and the heavy metal chromium along with additional physicochemical parameters were investigated in the filtrate. In wastewater from the tannery industry, the adsorption removal percentage for various physicochemical characteristics and heavy metals was calculated.

Results and discussion

The goal of this study was to analyse the physicochemical parameters of the tannery effluent of CETP Ranipet. There are reports of chromium recovery from tannery effluent by the adsorption process. But the major issues like TDS, TS, BOD, and COD are still unsolved misery to the tanneries. In the current investigation, the physicochemical characteristics of the untreated tannery effluent have revealed that it has high TDS, TS, BOD, COD, unpleasant odor, and dark colour.

The physicochemical properties of the effluent collected from CETP, Ranipet, India

Table 1: Physical and chemical analysis of tannery effluent

Parameters	Effluentcollected from CETP	Maximum tolerance limits for industrial effluents discharged(mg/L)**	
		Into Inland surface water	Into public sewers
Physical Parameters			
Colour	Slightly brown	Colourless	-
Odour	Disagreeable smell	Odourless	Unobjectionable
pH	7.21	5.5-9.0	5.5-9.0
Chemical Parameters			
Electrical conductivity (EC)(mS/cm)	27.9	0.288	-
Biochemical OxygenDemand (BOD) mg/L	1364	30	350
Chemical Oxygen Demand(COD) mg/L	3977	250	-
Total Dissolved Solids(TDS) mg/L	9700	2100	2100
Total Solids (TS) mg/L	14223	2200	-
Total Hardness (TH) mg/L	912	600	300
Turbidity(NTU)	312	10	5
Sodium (mg/L)	3847	-	60
Chromium (Cr) (mg/L)	1176	0.1	2.0

Values expressed as the mean of 6 individual values

**ISI Standards for disposal of industrial wastewater and CPCB.

The physicochemical parameters of the effluent collected from the CETP Ranipet, India are given in **Table – 1.** On comparison of the values obtained on analysis of the effluent with the values prescribed by ISI, for the effluent drained to Inland surface water, the parameters are very high that the partially treated effluent needs further treatment. The values exceed much above the prescribed tolerance limits values. Hence an attempt has been made through the current work to treat the effluent using naturally derived material using the cost-effective adsorption process. Operational parameters such as pH, adsorbent dosage, and residence time were varied, and the efficacy of the two selected materials such as algal biomass derived from brown algae *Sargassum whitti* and its biochar was investigated.

Treatment of tannery effluent using Algal Biomass and its Biochar

Effect of pH

Because pH prevents the formation of surface charges that are beneficial to ion retention and determine the ionic form of an element in a solution, it regulates the quantity of metal eliminated from the solution

(Souza et al., 2009). The effect of solution pH on the various physicochemical parameters and heavy metal chromium during adsorption using algal biomass and it's biochar are presented in **Tables – 2 and 3.**

Table 2: Effect of pH on the physicochemical parameters by algal biomass

Parameters	Raw Effluent	Effect of pH						
		2	3	4	5	6	7	8
Electrical Conductivity (mS)	27.9	21.7	19.9	19.5	18.9	18.5	16.7	18.9
Total Hardness(mg/L)	912	72	48	41	34	21	19	34
TDS (mg/L)	9700	2131	1145	527	468	296	99	173
TS (mg/L)	14223	3156	1431	1184	421	577	248	711
DO mg/L	0.3	1.5	2.1	2.7	3.1	3.2	3.6	2.4
BOD (mg/L)	1364	714	623	568	541	477	327	516
COD (mg/L)	3977	1471	1238	1062	915	815	616	815
Turbidity (NTU)	312	88	74	65	57	48	41	64
Sodium (mg/L)	3847	2517	2317	1769	1195	715	386	544
Cr (mg/L)	1176	815.4	691.4	318.92	255.38	175.82	44.34	82.77

Table 3: Effect of pH on the physicochemical parameters by algal biochar

Parameters	Raw Effluent	Effect of pH					
		3	4	5	6	7	8
Electrical Conductivity(mS)	27.9	16.5	16.2	15.3	15.2	15.2	15.1
Total Hardness(mg/L)	912	24	21	18	14	16	17
TDS (mg/L)	9700	671	388	251	115	51	112
TS (mg/L)	14223	823	798	755	421	399	721
DO mg/L	0.3	1.8	2.5	3.1	3.5	3.5	3.2
BOD (mg/L)	1364	574	494	411	385	271	322
COD (mg/L)	3977	937	880	721	688	562	611
Turbidity (NTU)	312	51	56	51	44	34	46
Sodium (mg/L)	3847	2114	1453	557	481	266	384
Cr (mg/L)	1176	617.48	228.66	121.54	98.15	21.12	28.66

To identify the optimum pH, the equilibrium batch process was conducted at different pH ranges from 3-8 and the results are given in **Table 1.** Each sample was adjusted for pH and maintained utilizing a 0.1N solution of HCL and NaOH. The algal biomass and its biochar adsorbents (1g) were treated with 100 mL of tannery water at respective pH for a period of 1 hour in a rotary shaker with a speed of 160 rpm. The results presented in **Tables 2 and 3** show that there is a decreasing trend observed in the values of almost all the physicochemical parameters till the pH reached the value 6 in both the adsorbents and the values started increasing at pH 7 and 8.

Less pH permits surface OH corporations to only take protons, enabling ligand alternate since H_2O is a less difficult ligand to get displaced from metal bonding sites than OH, and thus low pH increases ionic adsorption (Nithya and Sudha, 2017). The reduction in parameter removal at higher levels of pH can be accounted for by the deprotonation of acid groups, which substantially decreases the concentration of positive charges on the adsorbent's surface, and the competition between OH^- ions and chromium species for active points on the adsorbent (Cruz-Lopes et al., 2021). $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$ were generated by chromium, and the proportion of each species was determined by the chromium content and pH (Siraj et al., 2012).

Effect of dose of adsorbent

The dosage of the adsorbent is a crucial factor since it determines its capacity for adsorption (Ugwu et al., 2020). The influence of algal biomass and its biochar dosage was examined via various weights of 1–6 g with an optimal pH of 6 and the results are presented in **Tables 4 and 5.**

Table 4: Effect of adsorbent dose on the physicochemical parameters by algal biomass

Parameters	Raw Effluent	Effect of Adsorbent Dose (gms)					
		1	2	3	4	5	6
Electrical Conductivity (mS)	27.9	17.3	16.3	15.8	15.4	14.8	16.2
Total Hardness(mg/L)	912	45	25	21	18	16	18
TDS (mg/L)	9700	945	715	433	221	71	81
TS (mg/L)	14223	1572	1123	721	482	93	198
DO mg/L	0.3	2.6	2.9	3.1	3.7	3.9	3.9
BOD (mg/L)	1364	817	512	327	274	110	148
COD (mg/L)	3977	2091	1722	1527	1395	1145	1217
Turbidity (NTU)	312	119	72	61	51	28	26
Sodium (mg/L)	3847	1788	1431	1151	725	342	261
Cr (mg/L)	1176	258.82	159.62	83.66	38.67	22.11	21.96

Table 5: Effect of adsorbent dose on the physicochemical parameters by algal biochar

Parameters	Raw Effluent	Effect of Adsorbent Dose (gms)					
		1	2	3	4	5	6
Electrical Conductivity(mS)	27.9	15.6	15.6	15.4	15.1	14.2	15.9
Total Hardness(mg/L)	912	25	21	18	16	15	15
TDS (mg/L)	9700	925	694	312	189	69	67

TS (mg/L)	14223	1461	1011	698	471	88	167
DO mg/L	0.3	2.8	3.1	3.3	3.6	3.7	3.7
BOD (mg/L)	1364	719	417	298	236	98	96
COD (mg/L)	3977	1948	1688	1417	1318	1118	1106
Turbidity (NTU)	312	116	68	59	46	24	23
Sodium (mg/L)	3847	1781	1422	1139	716	312	250
Cr (mg/L)	1176	256.87	157.22	81.15	37.24	21.01	21.05

The maximum removal efficiency of physiochemical factors (for example reduction of COD by 71% (Algal biomass) and 72% (Algal biochar) and Chromium was 99.1% (Algal biomass) and 99.2% (Algal biochar)) was identified in 5g of dose for all parameters. There was not much decrease in the Chromium and other parameter levels after the dosage of 5g. It was discovered that as the dose of the composite was raised, the physicochemical characteristics and metal ion removal efficiency of the composite also increased. This was predicted since the greater the adsorbent dose in the solution, the more replaceable active sites for the ions are available. After a particular amount of the adsorbent was used, it demonstrated no further effective removal in adsorption (5gm) (Mia et al., 2020).

The COD and BOD removal efficiency increased for the biomass and biochar when increased from 1 to 5g. The maximum TS, Hardness, COD and BOD removal efficiency was achieved at optimum pH during the 60-minute treatment process. The rise in metal adsorption with greater adsorbent dosages might be attributed to the material's increased surface area and the abundance of active sites for adsorption.

Table 6: Effect of residence time on the physicochemical parameters by using algal biomass

Parameters	**Raw Effluent**	**Effect of Time (Hrs)**					
		1	**2**	**3**	**4**	**5**	**6**
Electrical Conductivity(mS)	27.9	17.3	15.4	15.2	14.9	14.6	14.4
Total Hardness (mg/L)	912	45	37	32	26	19	16
TDS (mg/L)	9700	945	726	445	129	99	96
TS (mg/L)	14223	1572	1231	789	505	204	201
DO mg/L	0.3	2.6	2.9	3.1	3.4	3.7	3.7
BOD (mg/L)	1364	817	342	278	203	154	151
COD (mg/L)	3977	2091	1641	1488	1347	1281	1276
Turbidity (NTU)	312	119	91	78	35	27	28
Sodium (mg/L)	3847	1788	1231	974	489	266	251
Cr (mg/L)	1176	258.82	131.65	72.67	49.88	24.07	21.32

Table 7: Effect of residence time on the physicochemical parameters by using algal biochar

Parameters	Raw Effluent	Effect of Time (Hrs)					
		1	2	3	4	5	6
Electrical Conductivity (mS)	27.9	15.6	15.3	15.1	14.8	14.4	14.2
Total Hardness (mg/L)	912	25	72	47	21	15	14
TDS (mg/L)	9700	925	693	416	116	89	89
TS (mg/L)	14223	1461	1172	769	496	201	199
DO mg/L	0.3	2.8	2.9	3.3	3.7	3.8	3.9
BOD (mg/L)	1364	719	295	216	199	147	141
COD (mg/L)	3977	1948	1611	1343	1281	1261	1261
Turbidity (NTU)	312	116	82	55	31	26	26
Sodium (mg/L)	3847	1781	1184	926	472	245	244
Cr (mg/L)	1176	256.87	119.7	61.71	41.88	22.32	20.81

The impact of time is considered a significant parameter for rapid adsorption and successful practical application of adsorbents. The impact of contact time on the adsorption process onto the algal biomass and algal biochar was studied from 1 to 6 hours of contact time.

Tables 6 and 75 showed the effect of time on the reduction of physiochemical parameters and metal removal using Algae and Biochar. The availability of empty sites on the surface of adsorbents until equilibrium might explain the quick rise in Chromium ion adsorption as contact duration increases (Santhosh and Dhandapani 2013).

The removal efficiency increased rapidly till 300 min for both the algal biomass and Algal biochar. Since the adsorption phase achieved equilibrium, there was no variation in equilibrium concentration during 300–360 minutes. The maximum amount of absorption happened in the initial stage because, in the initial period, the maximum number of active sites are available. This gave enough time for the adsorbate to interact with the surface of the adsorbent, which increases the adsorption performances and is expected to be constant (Bedada et al., 2020; Dursun, 2006).

The maximum removal percentage was obtained in 5 hours for all parameters. The highest removal efficiencies in the case of algal Biomass for different chemical parameters achieved were TDS, TS, BOD, COD, Turbidity, Total hardness, and Chromium 96 mg/L, 201 mg/L, 151 mg/L, 1276 mg/L, 16 mg/L, and 21.32 mg/L respectively. The highest removal efficiencies of different chemical parameters for Biochar achieved were TDS, TS, BOD, COD, Total hardness, and Chromium 89 mg/L, 199 mg/L, 141 mg/L, 1261 mg/L, 14 mg/L, and 20.81 mg/L respectively. Thus, Biochar showed slightly higher removal efficacy than biomass.

Table 8: Physical and chemical characteristics of effluent before and after treatment

Parameters	Raw Effluent from CETP	Treated with *Sargassum wightii*	Treated with Algal Biochar
Color	Brownish black	Colourless	Colourless
Odor	Unpleasant	Odourless	Odourless

pH	7.21	5	5
EC (mS/cm)	27.9	12.4	10.2
BOD (mg/L)	1364	290 (79)	120 (91)
COD (mg/L)	3977	1320 (67)	1120 (72)
TDS (mg/L)	9700	2260 (76)	1672 (83)
TS (mg/L)	14223	6240 (56)	4986 (65)
TH (mg/L)	912	28 (97)	22 (98)
Turbidity (NTU)	312	16 (95)	12 (96)
Sodium (mg/L)	3847	1720 (55)	1280 (67)
Chromium (mg/L)	1176	22.04 (98)	12.26 (99)

Values mentioned in brackets represent % reduction in the parameters compared to the raw effluent

EC-Electrical conductivity, BOD- Biological Oxygen Demand; COD-Chemical Oxygen Demand; TDS-Total Dissolved Solids; TS-Total Solids; TH-Total Hardness;

Consolidated values of the various physicochemical parameters and heavy metal chromium at optimum conditions of pH 6, adsorbent dosage 5gms, and contact time 5 hrs are presented in **Table 8.** The values give a clear understanding of how both the algal biomass and biochar show very good adsorptive behaviour, Among the two the biochar showed the best behaviour as an adsorbent.

Due to their high surface area as well as high binding affinity, microalgal cells have the ability to biosorb heavy metals very effectively (Chugh et al., 2022). Algal cells have the capability to bind metals with up to 10% of their total biomass. By complexing and attracting one another through electrostatic attraction, pollutants are bound to the surface of cells (Zohoorian et al., 2020) which require no energy (Chugh et al., 2022). Algae have three primary mechanisms that eliminate chromium: biosorption, bioaccumulation, and detoxification.

Durvillaea antartica was found to be able to adsorb 102.72 mg/g of chromium over the functional groups (hydroxyl, amino, methyl, and carboxylic) present on the extracellular layer of the brown algae at pH 5 in just under seven hours, as reported by Guarín-Romero et al. (Guarín-Romero et al., 2019). Similarly, the carbon derived by the pyrolysis of the algae is capable of removing heavy metal and other organic and Inorganic pollutants from water (Law et al., 2022; Michalak et al., 2019). The higher porous nature and greater surface area along with the large number of -OH and -COOH functional groups make the algal biochar an effective and efficient remediating agent of all types of pollutants and much more suitable for an effluent treatment.

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