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Effect of carbonization temperature in the production and utilization of green carbons for chromium (VI) removal

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Abstract

The paper has focused on the challenges/impacts of tannery effluent and evaluates the alternative treatment options used to treat, recover or recycle chromium from the waste water. The study on performance of vetiver root biomass (VRB) powder in this study investigates the production of using chemical activation in the removal of Chromium (VI) ion from aqueous solution in continuous mode using fixed bed column. Activated carbon (VRB-AC) was prepared from the pyrolysis at different temperatures (550 °C, 750 °C and 900 °C, 1 h) using impregnated with 1:1 KOH under inert atmosphere (Nitrogen). Resulting in an activated carbon with the highest surface area was chosen for subsequent studies and was characterized for its functional groups using FTIR spectrum. It can be concluded that adsorbent VRB prepared using a 1:1 impregnation ratio has the highest ... Spectrum. Thus, this study demonstrated the potential of using VRB as cheap and efficient raw materials to produce activated carbon for the treatment of industrial effluents.

Optimal conditions for the activation stage were obtained at 800 °C and a hold time of 1 h in the case of activation with carbon dioxide and at 700 °C and a hold time of 1 h in the case of activation with steam. The maximum functional groups were present in VRB achieved by Nitrogen activation were of 789m²/g and 0.3268 cm³/g.

The characterization of materials was done using TGA, BET, XRD, SEM, and FTIR. The SEM images of MIL-101 showed octahedral crystal structure and composite materials exhibited the same morphology as MIL-101(Cr) crystals on an activated carbon bed. The BET surface area of AC and AC/MIL-101(Cr)5% was measured 1096.83 and 2412.1 m²/g, respectively.

A comparative study has also been done on the adsorption capacity of VRB powder of various particle sizes. It was found that the metal uptake capacity (amount of removal) of Chromium (VI) ion decreased but the adsorption capacity (percentage of removal) increased with the decrease in the concentration of chromium (VI) in the initial sample solution. It was also observed that the order of metal uptake capacity & adsorption capacity of VRB powder passing through various sieve sizes for removal of Chromium (VI) removal was as follows: 150 micron > 300 micron > 600 micron.

Keywords: Adsorption, prawn shell waste, chromium (VI), continuous fixed-bed column experiments

1. Introduction

Tannery effluents are ranked as the highest pollutants among all industrial wastes. They are especially large contributors of chromium pollution. For instance, in India alone about 2000–3000 tone of chromium escapes into the environment annually from tannery industries, with chromium concentrations ranging between 2000 and 5000 mg/l in the aqueous effluent compared to the recommended permissible discharge limits of 2 mg/l^[1]. At high concentrations chromium is toxic, mutagenic, carcinogenic, and teratogenic. Chromium exists in oxidation states of +2, +3, and +6. The trivalent oxidation state is the most stable form of chromium and is essential to mammals in trace concentration and relatively immobile in the aquatic system due to its low water solubility. The hexavalent chromium is much more toxic to many plants, animals, and bacteria inhabiting aquatic environments. Their concentration in industrial wastewaters ranges from 0.5 to 270 mg/L^[2]. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L^[3, 4].

Several technologies are used to remove chromium from tanneries which include reduction followed by chemical precipitation^[5], ion exchange^[6], electrochemical precipitation^[7], reduction^[8], adsorption^[9], solvent extraction^[10], membrane separation^[11], concentration^[12], evaporation, reverse osmosis and bio-sorption^[13] and emulsion per traction technology^[14].

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On top of it, these methods being uneconomical, adsorption is considered most versatile and cost-effective method for removing any contaminants like heavy metal, especially, if combined with appropriate regeneration steps^[15, 16].

Utilization of agricultural waste biomass offers an interesting alternative to expensive treatment options based on its potential to be converted into activated carbon.

In the last decade, global consumption of activated carbon has grown by an average annual increase of 5.5% and it is forecasted to continue to do so at an even higher rate in the coming years (8.1% in 2018)^[1].

Since commercial activated carbons are often expensive (Baccar *et al.*, 2009), mainly due to extensive use of expensive precursors (e.g. coal), a large-scale effort has been conducted to use agricultural wastes for preparing cost-effective and advantageous activated carbon samples (Alslaibi *et al.*, 2013; Nowrouzi *et al.*, 2017; Singh *et al.*, 2013). On the other hand, in addition to the cost-effectiveness of many agricultural by-products or even being practically free at the processing sites, converting such waste materials into activated carbon which are then applied for the pollution control purposes is very interesting from the view point of environment and sustainability concept. Hence, in the last decades, many activated carbons have produced from different agricultural waste sources, like waste leaves, peels, pruned woods, nut shells, etc., and have applied to the removal of heavy metals, including lead, from waters and wastewaters. For example, Brudey *et al.* (2016) prepared three chemically activated carbons from lignocellulosic precursors, using sulfuric acid, and utilized them for lead adsorption. Demiral *et al.* (2014) used the chestnut shell for preparation of phosphoric acid-activated carbon to remove lead ions from water media. Nadeem *et al.* (2006) reported the removal of Pb(II) ions by adsorption on the steam activated carbon prepared from *M. oleifera* pod. Li *et al.* (2010). For example, Goel *et al.* (2005) treated commercial granular activated carbon with alkali sulphide to enrich its sulfur functional groups and use it in removing lead ions from aqueous solutions. Zubrik *et al.* (2017) employed a two-stage preparation method by activation of the firstly pyrolyzed biomass with KOH to prepare a more effective activated carbon for Cd(II) ion adsorption from water media. Wu *et al.* (2017) utilized Shengli lignite for obtaining a series of porous carbons (PCs) via hydrothermal carbonization and chemical activation with KOH for application as electric double layer capacitors. However, production of activated carbon via a two-stage chemical activation process, using two different chemical agents, has been rarely used by the researchers. A previous group study has shown that, due to its explosive characteristics at high temperatures, ammonium nitrate (NH₄NO₃) can be employed as a novel activating reagent for production of a surface engineered activated carbon with regular-shaped pores and high surface area, using pistachio wood wastes (PWAC) (Sajjadi *et al.*, 2018). In the present work, to improve the porosity and increasing the surface functional groups, pistachio wood wastes were subjected to a two-stage activation process using NH₄NO₃ and NaOH, respectively, as chemical activating agents, to produce a new activated carbon (PWAC-2) for Pb(II) ion removal from water bodies. The influence of physic-chemical parameters on the Pb(II) adsorption by PWA-2 was investigated comprehensively, using batch-mode adsorption experiment.

On the experimental field, since 2000, numerous studies have been conducted using a diverse range of precursor materials of residual biomass origin (corn, rapeseed, barley, almond shells, walnut, pistachio, peanut, acorn, rice, palm, olive pomace, cherry bones, datebones, bamboo, cotton stalks, Miscanthus, Sicyos, ...), being currently a field of study in growing expansion. With regards to the physical activation process, most published studies focus on the preparation of activated carbons from residual biomass sources, optimizing the conditions of the activation process with carbon dioxide or steam and the subsequent physical and chemical characterization^[11-13, 17-26].

Other studies, in a much smaller number, have analyzed the influence of the carbonization process conditions in the subsequent activation stage^[27-30]. Finally, for specific applications such as the adsorption of heavy metals, where it is important to increase the content of certain carboxyl, hydroxyl and amino functional groups that can be combined with the metals by ion exchange, Complexation or electrostatic attraction, studies have focused on the maximization of these groups.

There is a long history of the production of activated carbon (AC) (Yagmur *et al.*, 2008), which has shown excellent performance in a number of process applications. For example, AC has been used for the removal of heavy metals arsenic and chromium from aqueous solution (Asadullah *et al.*, 2014; Niazi *et al.*, 2018), and for the removal of pharmaceutical compounds from sewage effluent (Grover *et al.*, 2011). Similarly, the 4.00:1.00 (KOH: biomass) ratio produced promising results in most of the cases, with respect to different preparatory conditions (Luo *et al.*, 2018; Zhu *et al.*, 2014).

2. Materials and Methods

2.1 Preparation of Adsorbate Solution

The stock solutions of Cr(VI) of concentration 1000 ppm was prepared by dissolving 0.2828 grams of analytical grade of K₂Cr₂O₇ in 100ml of RO distilled water. The stock solution was further diluted with RO distilled water to desired concentration for obtaining the standard solutions for absorbance measurement. The sample solutions which were to be treated with the adsorbent were also prepared similarly by dissolving required quantity of the above mentioned salt in RO distilled water.

2.2 Preparation of Adsorbent

The vetiver root waste was obtained from an agricultural farm in Andhrapradesh after oil has been extracted from them. They were air-dried and powdered in a grinder roughly and were soaked in 1:1 KOH solution overnight and were dried in oven at 85 °C. Furthermore, they were inserted into a quartz reactor under constant N₂ flow of 50 ml/min at different temperatures (550 °C, 750 °C and 900 °C, 1 h). After cooling, they were washed with 1 M HCl solution to remove the adhered impurities. Thereafter washed thoroughly with distilled water in order to remove any excess acid present and dried at 105 ± 1 °C. The dry biomass was crushed into granules, sieved to different particle size less than 300 micron and then preserved in desiccators for use.

2.3 Measurement of Cr (VI) in Aqueous Solutions

There are some components within the VRB powder that may reduce the Cr(VI) to Cr(III). Therefore, oxidation of

Cr(III) within the samples to Cr(VI) is necessary before the analysis of each sample. Cr ions within the samples were oxidized by using potassium permanganate in acidic medium. The violet colour that forms as a result of the reaction between the Cr(VI) ions and 1,5-diphenyl carbazide in acidic medium, was measured by using JASCO V-530 UV/VIS - Spectrophotometer at 540 nm. The lowest limit of this method is 0.01 mg/L and the best suitable measurement range is 0.5-5.0 mg/L(ppm). For samples containing concentrations in the range 5.0 – 100.0 mg/L, the absorbance of pure $K_2Cr_2O_7$ solution at 313nm was taken as standard. Therefore, in order to obtain the unknown concentration of treated solutions, the samples were diluted before the measurements and measured values were multiplied by the dilution factor.

2.4 Column Studies

The fixed-bed column had 7.0 cm internal diameter and was 60 cm in height. The bed length used in every experiment was fixed at 50 cm. The bed was filled with the VRB powder up to the specified height of the column and different size of the adsorbent was used as specified for each experiment. In every experiment the metal solution of a known concentration was pumped at a fixed flow rate of 1 litre/min to the column filled with known bed height of adsorbent. The above fixed flow rate into the fixed column was maintained with the help of monitoring a bypass stream. The samples solution after passing through the adsorbent in the fixed bed column was again recycled back into the sample reservoir tank so that there is a continuous adsorption of Chromium ion. Samples for analysis of Chromium ion concentration were collected at a regular interval of 30 minutes from the bottom of the sample reservoir tank. The VRB powder used inside the fixed bed column was replaced by a fresh batch of VRB powder at the beginning of each of experiment. The metal uptake capacity (amount of removal of chromium ion) and the adsorption capacity (percentage of chromium ion removal) were calculated using the following equations:

Metal Uptake Capacity = Initial Chromium ion conc. – Final Chromium ion conc.

Adsorption Capacity (%) = (Metal Uptake Capacity X 100) / Initial Chromium ion conc.

Table 8: Comparison of Conc. of solution at different time intervals (Initial solution conc. = 500ppm)

S. No	Time (in hrs.)	Adsorbent size: 150 micron I.S Sieve	Adsorbent size: 300 micron I.S Sieve	Adsorbent size: 600 micron I.S Sieve
		Concentration (in ppm)	Concentration (in ppm)	Concentration (in ppm)
1	0.5	464.1	468.9	476.2
2	1.0	437.9	450.2	459.1
3	1.5	419.8	436.1	447.7
4	2.0	404.7	423.8	439.0
5	2.5	391.9	414.1	432.2
6	3.0	380.6	405.9	425.8
7	3.5	372.3	397.7	422.7
8	4.0	364.5	392.8	420.9
9	4.5	360.4	387.9	419.2
10	5.0	356.3	385.3	417.1
11	5.5	352.9	382.2	415.2
12	6.0	351.1	380.0	413.3
13	6.5	349.2	377.9	410.9
14	7.0	347.9	377.1	410.0
15	7.5	346.8	375.9	409.1
16	8.0	345.9	375.1	407.9

3. Results and Discussion

3.1 Study of Adsorption Capacity

3.1.1 Effect of Activation Temperature (550°)

The Bed height of adsorbent employed was 50 cm for a fixed flow rate of solution through the bed was 10/min. At a temperature of activation 550 °C and the initial Cr^{+6} solution of 0.2 N and a concentration is 10 ppm sample was prepared.

Table 1: Effect of temperature of activation on VRB-AC (550°C)

S. No	Time (in hr.)	Concentration (in ppm)	S. No	Time (in hr.)	Concentration (in ppm)
1.	0.5	10.1	9.	4.5	3.9
2.	1.0	9.1	10.	5.0	3.4
3.	1.5	8.1	11.	5.5	2.9
4.	2.0	7.2	12.	6.0	2.4
5.	2.5	6.2	13.	6.5	2.2
6.	3.0	5.4	14.	7.0	2.0
7.	3.5	4.8	15.	7.5	1.9
8.	4.0	4.4	16.	8.0	1.8

Calculations

Metal Uptake Capacity = 12ppm – 1.8ppm = 10.2ppm

Adsorption Capacity = (10.2 x 100)/12 = 85%

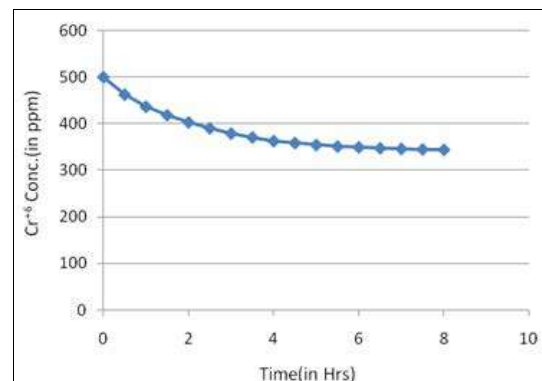


Fig 7: Cr^{+6} Conc. Vs Time plot (Adsorbent size = 300 micron I.S Sieve, Initial solution conc. = 12ppm)

3.2 Study on Effect of Size on Adsorption Capacity

Bed height of adsorbent = 50 cm

Flow rate of solution through the bed = 1 litre/min

Initial Cr^{+6} solution conc. = 500ppm (14.14 gm of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Calculations

For 150 micron LS Sieve VRB powder

Metal Uptake Capacity = $500\text{ppm} - 345\text{ppm} = 155\text{ppm}$

Adsorption Capacity = $(155 \times 100)/500 = 30.8\%$

For 300 micron LS Sieve VRB powder

Metal Uptake Capacity = $500\text{ppm} - 375\text{ppm} = 125\text{ppm}$

Adsorption Capacity = $(125 \times 100)/500 = 25\%$

For 600 micron LS Sieve VRB powder

Metal Uptake Capacity = $500\text{ppm} - 408\text{ppm} = 92\text{ppm}$

Adsorption Capacity = $(92 \times 100)/500 = 18.4\%$

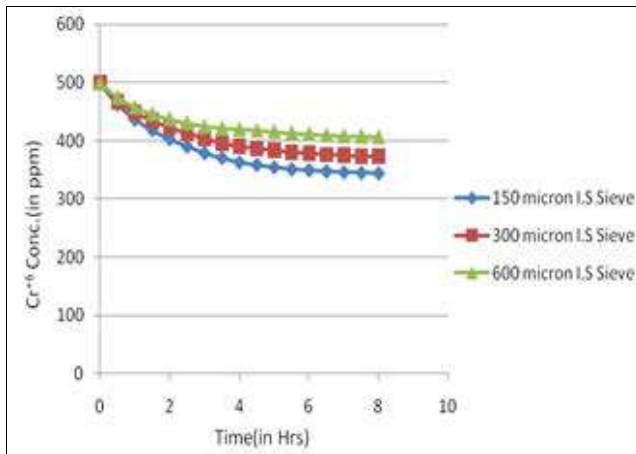


Fig 8: Comparison of Cr^{+6} Conc. Vs Time plot (Initial solution conc. = 500ppm)

4. Conclusion

Continuous fixed bed column studies were performed for removal of Chromium (VI) ion from water using various particle sizes of VRB powder. The study indicated the suitability of the adsorbent for removal of Chromium (VI) from aqueous solutions. The selected adsorbent may be viewed as a useful material while considering the economic aspects of wastewater treatment. The metal uptake capacity decreases with decrease in the initial concentration of Cr^{+6} solutions. However, the percentage of removal or the adsorption capacity is found to increase with lower initial concentration of chromium. The VRB powder particles of size 300 micron required 7 fixed bed columns of fresh VRB powder (run for 8 hours over each bed) for the removal of Chromium ion from 500ppm to a value of as low as 12ppm. The observed order of metal uptake capacity as well as adsorption capacity of Cr^{+6} for VRB powder of different LS sieve sizes were as follows: 150 micron > 300 micron > 600 micron. These experimental studies on the specified adsorbent would be quite useful in developing an appropriate technology for the removal of Cr^{+6} ions from contaminated industrial effluents.

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