Preparation and Characterization of Activated Carbons from *Parthenium* Biomass by Physical and Chemical Activation Techniques

RAJESHWARI SIVARAJ*, VENCKATESH RAJENDRAN[§]
and G. SANGEETHA GUNALAN

Department of Biotechnology, School of Life Sciences,
Karpagam University, Eachanari, Coimbatore-641021, Tamilnadu, India.

[§]Faculty of Chemistry, Government Arts College,
Udumalpet-642126, Tamilnadu, India.

rajeshwarishivaraj@gmail.com

Received 21 January 2010; Accepted 15 March 2010

Abstract: *Parthenium hysterphorous* (Linn), a perennial weed of no known beneficial use was introduced as a containment of food grains imported from US with P1480 scheme. The colonization efficiency of the weed was much higher than other indigenous weeds resulting in the reduction of cultivable areas of agricultural lands. Therefore, attention was focused to find out the potential use of its biomass. In the present study the preparation and characterization of activated carbons by physical and chemical activation methods are reported and aims to prepare relatively well developed porous activated carbons as well as study various conditions and parameters that were involved during the process. Among the carbons prepared ZnCl₂ impregnated carbon at the ratio of 1 was found to possess the characteristic features of an efficient adsorbent. Experimental results showed that pyrolytic and activation conditions leading to various final average temperatures had significant effect on the properties of activated carbons prepared.

Keywords: *Parthenium hysterphorous* (Linn), Activated carbon, Physical and Chemical activation, Characteristics, Impregnation.

Introduction

Pollution of water bodies is on increase in developing countries like India in view of direct release of untreated or partially treated industrial wastewater. Various treatment techniques have been developed involving or combining one or more of physical, chemical and biological methods. Unlike in developed countries neither enforcement of environmental laws by governmental agencies nor compliance to them by the industries is up to the level required to protect aquatic environments. In India most of the polluting industries being small-scale industries, cheap but effective technologies are being developed so as to fit in their budget and one such treatment technology involves the use of activated carbon.

However, activated carbon prepared from conventional raw materials such as bituminous coal and peat are also expensive. Attempts have been made to prepare activated carbon from cheap and readily available materials. To date, there had been an increasing interest in the production of activated carbon from agricultural by products and industrial wastes¹.

Parthenium hysterophorus (Linn), a perennial weed of no known beneficial use was introduced as a containment of food grains imported from US with PL480 scheme². The colonization efficiency of the weed was much higher than other indigenous weeds resulting in the reduction of cultivable areas of agricultural lands. Further, efforts taken to check their proliferation and eradication became a futile exercise in India. Therefore, attention was focused to find out potential use of its biomass. In this context, this paper presents the methods of preparation of carbon from *Parthenium* biomass, its yield and its characteristics for potential applications in the removal of pollutants of diverse nature from polluted waters.

Experimental

Parthenium plant was collected from fallow lands in and around Coimbatore City, Tamilnadu, India. It was cut into small pieces (93 mm size app), dried in sunlight until all the moisture was evaporated. The dried material was used for the preparation of activated carbon using physical and chemical activation methods. All the reagents used were of analytical reagent grade and were obtained from SD's, Qualigen's and Merck's, Bombay, India.

Nature of the adsorbent

SEM analysis of the adsorbent was performed at the Institute of Materials, University of Nantes, The Nantes, and France.

Preparation of activated carbon

Physical activation

Parthenium was completely filled in a copper vessel of 36×2.8 cms and covered with a tight fitting lid to avoid contact with atmospheric air except with the air trapped in the voids of the material being activated. This setup was placed in a muffle furnace at 5 different terminal temperatures ranging from 400-800 °C, respectively for 1. After cooling, the material was taken out and stored in plastic containers and used for further studies.

Chemical activation with zinc chloride

Carbon were prepared from *parthenium* plant using ZnCl₂ as an active agent at impregnation ratios from 0.0625 - 1.00 where impregnation is defined as

$$\text{Impregnation ratio} = \frac{\text{Weight of the active agent used (ZnCl}_2\text{)}}{\text{Weight of the carbonizing material (Parthenium)}}$$

Activated carbon was prepared as described in the physical activation method after the material was impregnated with ZnCl₂ at 700 °C for 1h in the boiling solution of the later³. On cooling the excess of ZnCl₂ on the activated carbon particles were leached out by immersing it in 1M HCl solution for about⁴ 24 h. It was then repeatedly washed with hot distilled water until all chlorides had disappeared from the wash water. The material was subsequently oven dried at 80 °C for 6 h and stored in airtight plastic containers.

Chemical activation with acids

Conc. H₂SO₄, HCl, HNO₃ and H₃PO₄ were used for the preparation of activated carbon from *parthenium* plant. One part of *parthenium* material was mixed with 1.5 part acid and kept⁵ in a muffle furnace for 14 h at 120 °C. The carbonized material was washed with distilled

water several times to remove the free acid and soaked in 1%(w/v) NaHCO_3 solution overnight to remove any residual acid⁶. The material was then washed with double distilled water until the pH of the filtrate was well above 5.0. The material was dried at 80 °C for 6 h and stored in airtight plastic containers.

Chemical activation with H_2SO_4 and ammonium persulphate ($\text{NH}_4\text{S}_2\text{O}_8$)

Ammonium persulphate, an activating agent was used with H_2SO_4 in the preparation of activated carbons⁷. In this method 1 part of the material and 1.5 part of H_2SO_4 were mixed with 0.4 parts of Ammonium persulphate⁸ and kept in a muffle furnace at 120 °C for 14h and the procedure was repeated.

Results and Discussion

The yield of parthenium carbon under different activation methods is given in Table 1.

Table 1. Carbon yield

S. No.	Physical (thermal) activation	
	Temperature, °C	Yield, %
1.	400	48.74
2.	500	45.39
3.	600	45.13
4.	700	38.69
5.	800	36.00
	Chemical activation	
	Zinc chloride impregnation ratio	Yield, %
6.	0.0625	30.98
7.	0.125	36.66
8.	0.25	36.94
9.	0.5	39.07
10.	1.0	45.19
	Acid	Yield, %
11.	H_2SO_4	70.00
12.	HCl	47.89
13.	HNO_3	37.65
14.	H_3PO_4	46.71
15.	$\text{H}_2\text{SO}_4 + \text{NH}_4\text{S}_2\text{O}_8$	72.00

A decrease in the yield of carbon as the terminal temperature from 400 °C to 800 °C was observed and is consist with the finding that higher the pyrolytic temperature, lower is the yield owing to the progressive loss of organic matter⁹. In Zinc chloride activation the percent yield increased (30.98%-45.19%) with increasing impregnation ratio from 0.0625-1.00. In acid activation the order of percentage of yield was.

Among the various methods of activation, the carbon yield was highest in acid activation¹⁰. The inhibition of tar formation and increased pyrolytic decomposition are considered as reasons for higher yield of carbon in both zinc chloride and acid activation¹¹. However, in the latter the degree of such processes may be comparatively higher. Retention of a greater proportion of low molecular weight scission products in the carbon residue has also been considered as the reason for the enhanced yield of carbon in the case of Zinc chloride activation¹².

Characteristics of carbon

The physical and chemical characteristics of carbons are summarized in Tables 2-4.

Table 2. Characteristics of *Parthenium* activated carbon prepared by physical activation (Thermal)

Parameter	Carbonization temperature, °C				
	400	500	600	700	800
pH	8.330	8.440	8.750	8.770	8.950
Conductivity, $\mu\text{S}/\text{cm}$	1.860	1.860	2.470	2.530	2.670
Specific gravity	0.305	0.570	0.593	0.632	0.884
Bulk density, g/mL	0.233	0.194	0.193	0.182	0.180
Porosity, %	23.610	59.120	60.540	62.500	73.080
Decolorizing power, mg/g	12.000	12.750	13.500	13.500	14.250
Ion exchange capacity, (mequ/g)	Nil	Nil	Nil	Nil	Nil
Moisture, %	2.600	2.100	2.000	1.250	1.000
Volatile Matter, %	20.000	16.570	12.130	12.190	10.810
Fixed Carbon, %	76.500	80.900	81.020	81.200	82.800
Ash, %	3.630	5.110	6.020	6.200	6.670
Surface Area (M^2/g)	155.910	430.610	498.440	302.070	292.450
Iron, W/W, %	1.200	1.400	1.300	1.300	1.300
Silica, W/W, %	Nil	Nil	Nil	Nil	Nil
Sodium, W/W, %	5.000	5.200	5.200	5.100	5.200
Potassium, W/W, %	3.400	3.600	6.300	3.600	3.400
Phosphorus, W/W, %	0.010	0.010	0.010	0.010	0.010
CCl_4 activity, W/W, %	0.030	0.160	1.140	2.550	2.150
Phenol adsorption capacity, mg/g	0.480	0.640	1.810	1.990	3.000
Matter soluble in water, %	3.900	3.470	5.100	3.250	3010.000
Matter soluble in 0.25M HCl, %	5.410	9.400	11.020	13.400	11.170

Table 3. Characteristics of *Parthenium* activated carbon prepared chemical activation (Acids)

Parameter	H_2SO_4	HCl	HNO_3	H_3PO_4	H_2SO_{4+} $\text{NH}_4\text{S}_2\text{O}_8$
pH	8.170	5.130	5.290	5.020	5.850
Conductivity, $\mu\text{S}/\text{cm}$	0.410	0.140	0.270	0.120	0.190
Specific gravity	0.760	0.628	0.605	0.685	0.660
Bulk density, g/mL	0.202	0.172	0.149	1.144	1.420
Porosity, %	73.420	79.030	71.570	78.250	78.480
Decolorizing power, mg/g	13.200	19.050	21.850	20.550	30.000
Ion exchange capacity (mequ/g)	0.250	0.230	0.270	0.280	0.450
Moisture, %	3.300	2.200	1.700	3.700	1.200
Volatile matter, %	57.330	50.334	59.480	51.750	57.010
Fixed Carbon, %	31.200	39.900	31.700	35.100	34.000
Ash, %	8.170	7.566	7.120	9.450	9.420
Surface Area (M^2/g)	680.000	252.530	162.270	475.050	760.570
Iron, W/W, %	1.200	1.400	1.300	1.100	1.200
Silica, W/W, %	Nil	Nil	Nil	Nil	Nil
Sodium, W/W, %	10.090	2.800	7.500	6.700	5.900
Potassium, W/W, %	0.473	0.653	1.007	0.227	0.240
Phosphorus, W/W, %	BDL	BDL	BDL	BDL	BDL
CCl_4 activity, W/W, %	1.190	0.350	1.200	0.150	1.350
Phenol adsorption capacity, mg/g	0.700	1.770	1.000	1.700	2.100
Matter soluble in water, %	3.100	1.430	1.630	0.415	2.510
Matter soluble in 0.25M HCl, %	2.480	2.860	4.880	2.080	0.500

Table 4. Characteristics of *Parthenium* activated carbon prepared by chemical activation (ZnCl₂)

Parameter	ZnCl ₂ impregnation ratio				
	0.0625	0.125	0.25	0.5	1.0
pH	6.570	6.550	6.440	6.390	6.330
Conductivity, $\mu\text{S}/\text{cm}$	0.160	0.130	0.210	0.210	0.180
Specific gravity	0.714	0.801	0.810	0.812	0.822
Bulk density, g/mL	0.182	0.202	0.212	0.221	0.222
Porosity (%)	74.520	74.400	73.840	72.780	72.990
Decolorizing power, mg/g	14.250	18.000	26.550	27.450	46.650
Ion exchange capacity (mequ/g)	0.120	0.150	0.350	0.400	0.610
Moisture, %	1.100	2.700	4.200	5.100	6.230
Volatile Matter, %	11.400	12.400	12.900	14.000	11.700
Fixed Carbon, %	87.500	84.900	84.900	75.700	87.000
Ash, %	7.380	6.780	6.750	6.680	6.650
Surface Area, M ² /g	1089.260	982.420	941.040	872.880	839.880
Iron, W/W, %	1.100	1.100	1.100	1.100	1.200
Silica, W/W, %	Nil	Nil	Nil	Nil	Nil
Sodium, W/W, %	1.600	1.400	1.500	1.400	1.600
Potassium, W/W, %	1.120	1.120	1.180	1.120	1.100
Phosphorus, W/W, %	BDL	BDL	BDL	BDL	BDL
CCl ₄ activity, W/W, %	0.480	0.980	0.980	0.990	1.050
Phenol adsorption capacity mg/g	2.500	4.300	6.500	7.000	7.100
Matter soluble in water, %	0.810	1.990	3.290	3.570	3.650
Matter soluble in 0.25M HCl, %	10.520	12.390	12.330	12.040	9.320

BDL – below detection limit

In general the porosity of activated carbons was around 65% and 75% for thermal and zinc chloride activated carbons, respectively. For thermal and zinc chloride activated methods, the bulk density, decolorizing power, CCl₄ activity and phenol adsorption capacity generally increased with increase in temperature and zinc chloride impregnation ratio, respectively. Higher decolorizing power, ion exchange capacity and phenol adsorption capacity of the carbons imply that, they are more suitable for adsorption of organic substances.

Surface area showed an increasing trend up to the temperature of 600 °C (155.91 M²/g - 498.44 M²/g at 800 °C). Similar results were reported for Ajax activated carbon^{13,14}. According to them micropore volume increases with increase in activation temperature due to enlargement or drilling of existing pores and narrowing of pores due to shrinkage of carbon particles causes a decrease in the surface area. With increase in the impregnation ratio of ZnCl₂, the surface area showed an increasing trend (839.88 M²/g -1089.26 M²/g). Normally the porous structure is better in the case of chemical activation and the pore size distribution with the degree of impregnation, larger is the pore diameter of the carbon with consequent increase in the surface area¹⁵. The surface area of carbon prepared by acid activation decreased in the following order.

Among the carbons prepared, ZnCl₂, impregnated carbon at the ratio of 1.0 was found to exhibit the maximum surface area of 1089.26 M²/g. The bulk density decreased with increasing activation temperature. The observed decrease in the bulk density may be, as reported, due to the pore system becoming larger with increasing activation, a decrease in the apparent density and the constant real density of carbon^{16,17}. The bulk density of the acid treated carbons was in the order and

The bulk density of ZnCl_2 activated carbons increased with increase in the degree of impregnation. The data pertaining to matter soluble in water (very low in all activated carbon) indicated that the carbons exhibit very low leaching properties suggesting that desorption of impurities from the carbon will be insignificant in aqueous solution¹⁸. The iron content is considerably lower in all the carbons implying that these carbons can be used in the treatment of water without the problem of iron being leached into the treated water. In view of this and the observed higher fixed carbon content, surface area, decolorizing power, phenol adsorption capacity and iron exchange capacity, the activated carbon prepared by the ZnCl_2 impregnation at the ratio of 1 was subject to SEM analysis to assess its nature Figure 1 and the results showed that the activated carbon is amorphous in nature. Amorphous carbons have larger surface area compared to carbons with more crystalline and well-defined structure. Larger the surface area, greater will be its adsorption capacity.

Figure 1. SEM analysis of ZnCl_2 activated carbon sample.

Conclusion

In view of the high adsorbing capacity and characteristics activated carbon prepared from *Parthenium* plant can be effectively used for the removal of pollutants from wastewaters. As *Parthenium* is a noxious weed, its utilization serves the dual purpose of simultaneous eradication for better utilization.

References

1. Robinson T, Chandran B and Nigam P, *Bioresour Technol.*, 2002b, **85**, 119-124.
2. Kavita G and Nagendra B, *Indian J Ecol.*, 2000, **27**, 177-180.
3. Kadriivel K, Palanivel M, Kalpana R and Rajeswari S, *Biosource Technol.*, 2000, **74**, 263-265.
4. Calahomo V C, Garica A B, Barrera C P, Garica M J B and Gómez Corzo M, *Bioresources Technol.*, 1993, **44(3)**, 229-233.
5. Khattri S D and Singh M K, *Indian J Chem Technol.*, 1999, **6**, 112-116.
6. Rodriguez R F, Lopez-G D J and Berenguer C, *Carbon*, 1982, **20**, 513-518.
7. Aloko D F and Adebayo G A, *J Eng Appl Sci.*, 1984, **1**, 211-222.
8. Rengaraj S, Banumathi Arabindo and Murugesan V, *J Sci Ind Res.*, 1998, **57**, 129.
9. Ahmadpor A and Dodd, *Carbon*, 1995, **33**, 1393-1398.
10. Bansal R C, Donnet J B, Stoeckli F and Marcel D, Active carbon, Inc., 1988, New York.
11. Hitchcock S J, Mc Enaney B and Watling S J, *J Chem Tech Biotechnol.*, 1983, **33A**, 257-163.
12. Huiping Zhang, Ying Yan and Lichun Yang, *Adsorption*, 2010, **16(3)**, 161-166.
13. Ahmadpour A and Do D D, *Carbon*, 1995, **33(10)**, 1393-1398.
14. Lopez-G D J, Valenzuela C C, Navarette G A and Gomez S V, *Carbon*, 1980, **18**, 413-428.
15. Luis K O and Luis K S, *Bioresource Technol.*, 2000, **40(3)**, 215-219.
16. Rengaraj S, Banumathi A and Murugesan B, *Indian J Chem Technol.*, 1999, **6**, 1-4.
17. Meyer V, Carlsson F H H and Oellermann R A, *Wat Sci Technol.*, 1992, **26**, 1205-1211.
18. Nasser M M and El-Geundi M S, *J Chem Tech Biotechnol.*, 1991, **50**, 257-264.