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Characterization and adsorption studies of activated carbon and polymer coated sawdust for the removal of various pollutants from industrial wastewater

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ABSTRACT

Activated Carbon of high adsorption capacities were prepared from Casuarina by various physical and chemical processes followed by activation at 800ºC. The physico-chemical characteristics such as moisture content, volatile content, Specific gravity, Porosity, bulk density, pH, conductivity, Methylene blue number, iodine number were also investigated in order to understand the adsorptive capacity of activated carbon prepared from the agricultural waste. The present study analyses the feasibility of removing colour and reducing various water quality parameters like BOD, COD, alkalinity, etc., from the effluent samples collected from different industries using activated carbon (CAC) and polypyrrole coated sawdust (PPy/SD) prepared from Casuarina as adsorbents. Several other parameters such as chlorides, sulphates, TDS, pH and hardness present in the effluent sample before and after adsorption were also measured and were found to be in par with the permissible limit.

Keywords: Activated carbon, adsorption, Colour Removal, saw dust, effluent.

INTRODUCTION

Environmental pollution due to industrial effluents is of major concern because of their toxicity and threat for human life and the environment. The discharge of textile effluents to the water bodies has raised much concern because of potential hazards associated with the entry of toxic components into the food chains of human and animals. Synthetic dyes are extensively used for dyeing and printing in a variety of industries. Dyes are used in many industries such as carpets, paper, plastics, food and textile in order to colour their products [1]. Over 10,000 dyes with an annual production over $7x10^5$ metric tons worldwide are commercially available and 5-10% of the dye stuff is lost in the industrial effluents [2]. Therefore there is a need to remove dyes before effluent is discharged into receiving water bodies. The most popular treatment methods for textile wastewater are combinations of biological treatment, chemical coagulation, chemical oxidation, membrane separation, electrochemical treatment, filtration, hydrogen peroxide catalysis, reverse osmosis and activated carbon adsorption [3-5].

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances [6]. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes. Adsorption by activated carbon has a greater tendency for the removal of dyes without introducing any impurities.

Conducting polymer or green composites are viable alternative for the existing waste water treatment technologies. One efficient way of increasing the adsorption capacity of saw dust is by the polymerization of monomer on the surface of saw dust. In recent years, conducting electro active polymers such as polypyrrole has received great attention due to their electrical conductivity and electro activity [7-9].

In the present study an attempt has been made to study the characterisation of activated carbon and to investigate the use of activated carbon and polymer coated sawdust as adsorbents for the removal of pollutants from textile effluent.

MATERIALS AND METHODS

2.1 Preparation of Activated Carbon

The seeds and branches of Casuarina were collected and cut into small pieces (2 cm), washed with distilled water and dried in sunlight for 10 days. The dried material was soaked in a boiling solution of 40% H_3PO_4 for 1 hour and kept at room temperature for 24 hours. After 24 hours, the wood material was separated, air dried and carbonized in muffle furnace at 400 °C. The carbonized material was then powdered and activated in a muffle furnace at 800 °C for a period of 10 minutes. After activation, the material was repeatedly washed with plenty of distilled water. The characteristics of activated carbon are analyzed as per the standard procedures [10, 11] and are given in Table 1.

2.2 Carbonization procedures [12]

The activated carbon were prepared by the following method and listed in Table 1.

2.2.1 Direct pyrolysis

The precursor material was subjected to carbonization at 400 °C, powdered well and finally activated at a temperature of 800° C for a period of 10 minutes. After activation, the material was repeatedly washed with plenty of distilled water.

2.2.2 Carbonization with $CaCl_2$

The material to be carbonized was impregnated with a boiling solution of 10% $CaCl_2$ for 2 hours and soaked in the same solution for 24 hours. At the end of 24 hours, the excess solution was decanted off and air dried. Then the material was carbonized in muffle furnace at 400 °C. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes. Then the material was washed with plenty of water to remove residual acid, dried and powdered.

2.2.3 Carbonization with Sulphate salts

The precursor material was soaked in 10% solution of sodium sulphate for the period of 24 hours. After impregnation, the liquid portion was decanted off and then dried. The dried mass was then subjected to carbonization process in a muffle furnace at 400 °C .The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes.

2.2.4 Carbonization with H_3PO_4

The precursor material was impregnated with boiling solution of 10% H_3PO_4 for 2 hours and soaked in the same solution for 24 hours. At the end of 24 hours, the excess solution decanted off and air dried. Then the material was carbonized in muffle furnace at 400 °C. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes. The material was then washed with plenty of water to remove residual acid, dried and powdered.

2.2.5 Carbonization with KOH

The dried precursor material was soaked with 10% KOH solution for 24 hours. At the end of 24 hours, the excess KOH solution was decanted off and air dried. Then the material was subjected to carbonization process in a muffle furnace at 400 °C for 2 hours. The dried material was powdered and activated in a muffle furnace at 800° C for a period of 10 minutes. After activation, the carbon was washed with 4N HCl to remove the residual KOH. Then the material was washed with plenty of water, dried and stored.

2.2.6 Acid process

The dried material was treated with excess of hydrochloric acid and sulphuric acid respectively. Charring of these materials occurred immediately, accompanied by evolution of heat and fumes. When the reaction subsided, the mixture was left in an air oven maintained at 140-160 °C for a period of 24 hours. At the end of this period, the product was washed with large volume of water to remove free acid, dried at 110 °C and finally activated at 800° C.

2.2.7 Dolomite Process

The dried material which is to be carbonized was taken over calcium carbonate bed and the upper layer of the precursor was also covered with a layer of calcium carbonate. The entire material was carbonized at 400 °C, powdered well and then was activated at 800° C. After activation, the material was washed with excess of water to remove calcium carbonate and dried at 110° C.

2.2.8 Characterization of the carbons

Conductivity and pH were analyzed using Elico make pH meter (model L1-120) and conductivity meter (model M-180) respectively. Moisture content (%) by mass, ash content (on dry basis) %) by mass, volatile matter, fixed carbon content, bulk density, specific gravity, porosity, iodine number, methylene blue number, matter soluble in water, matter soluble in acid were analyzed as per standard procedures and the values are listed in Table 2.

2.3 Preparation of Poly pyrrole coated sawdust

Saw dust prepared from Casuarina was used for the preparation of polymer coated adsorbent. The saw dust was first washed with distilled water in order to remove the impurities and finally dried at 333 K for 2 hours. In order to prepare polymer coated saw dust, 5.0 g of saw dust was immersed in 50 ml of 0.20M freshly distilled pyrrole solution for 12 hours before polymerization. 50 ml of 0.5 M $FeCl_3$ as the oxidant solution was added into the mixture gradually and the reaction was allowed to continue for 4 hours at room temperature. The polymer coated saw dust was filtered, washed with distilled water, dried in an oven at 55-60^0 C and sieved before use [13].

2.4 Collection of effluent samples

The effluent samples from dyeing industries were collected from the outlet of various dye processing unit immediately after the completion of the dyeing process before discharging the effluent into the common collection tank.

2.5 Analysis of samples

The effluent samples were analyzed to measure their pH, electrical conductivity, dissolved oxygen, BOD, COD, hardness, alkalinity and TDS using standard methods.

2.6 Experimental setup

The effluent samples were taken in a clean, dry 200 ml conical flask and kept in an orbital shaker at a temperature of 30^{0}C and 150 rpm. Adsorbents namely CAC and PPy/SD which is pre-prepared is added into the effluent sample with a dosage rate of 2 grams per 50 mg/L. The flasks are initially stirred with a glass rod for mixing and are shaken in orbital shaker for 2 hours. Samples were drawn and checked for pH, conductivity, TDS, BOD, COD, chloride, sulphate as per APHA standards. All the tests are done in triplicate and the concordant values were taken for the result comparison. For the entire study, analytical grade chemicals were used.

RESULTS AND DISCUSSION

3.1 General Properties of Activated carbon

The pH of CAC1, CAC2, CAC3, CAC5, CAC6 and CAC7 are near neutral which will be helpful for the treatment of all types of dyes and wastewater. The carbon obtained could also be used for the purification of drinking water. CAC4, CAC8 and CAC9 carbons are found to be slightly basic in nature. This may be due to the presence of residual salts in the carbon. No marginal variation was noticed in the conductivity values of carbons prepared in all the processes. This may be due to the presence of uniform exchangeable site on the porous surface of the activated carbon. From Table 2, the moisture content was found to be higher in the case of carbons obtained by KOH and dolomite process.

Even though moisture content of the carbon has no effect on its adsorptive power, it dilutes the carbon which necessitates the use of additional weight of carbon during treatment process. Ash content generally gives an idea about inorganic constituents associated with carbon obtained by different carbonization methods. The ash content values from Table 2 indicate that the overall ash content for all varieties of carbon prepared shows a lesser value. This may be attributed to lower inorganic content and higher fixed carbon.

Volatile matter is due to the presence of highly porous organic compounds present in the raw material. High value of ash and volatile matter reduces the quantity of fixed carbon. From the data it was clear that all carbons have a good percentage of fixed carbon. Solubility studies of carbon in acid and water were performed to evaluate the amount of impurities present in the carbon prepared by different carbonization process.

The solubility studies were performed since the presence of impurities in the carbon may affect the expected quality of the treated water during treatment. From Table 2, the data pertaining to the matter soluble in water and acid indicates that all carbons contain very less amount of impurities. Porosity is the main factor for increasing the adsorptive power of an activated carbon. Porosity is also interrelated to the bulk density and specific gravity of activated carbon. From Table 2, it is clearly seen that CAC5 has higher porosity than all the other carbons.

Table 1 - List of Activated carbons prepared from Casuarina

S. No	Activated carbon	Preparation method
1.	**CAC1**	Direct Pyrolysis
2.	**CAC2**	$CaCl_2$impregnation
3.	**CAC3**	Na_2SO_4impregnation
4.	**CAC4**	Na_2CO_3 impregnation
5.	**CAC5**	H_3PO_4 impregnation
6.	**CAC6**	HCl process
7.	**CAC7**	H_2SO_4, process
8.	**CAC8**	KOH impregnation
9.	**CAC9**	Dolomite process

Table 2 - Physico-chemical characteristics of activated carbon

S.No	Properties	Activated Carbon								
		AC1	*AC2*	*AC3*	*AC4*	*AC5*	*AC6*	*AC7*	*AC8*	*AC9*
1	pH	*6.7*	*6.4*	*7.2*	*8.4*	*6.8*	*7.3*	*7.1*	*8.2*	*7.8*
2	Conductivity, mS cm -2	0.38	0.29	0.42	0.54	0.12	0.25	0.25	0.19	0.26
3	Moisture content, %	10.1	15.4	15.1	16.0	16.3	14.2	18.2	25.5	18.8
4	Ash, %	17.4	18.6	11.6	16.1	10.3	15.2	16.6	12.6	14.8
5	Volatile matter, %	13.3	6.6	10.6	11.3	5.7	12.6	7.3	18.2	11.3
6	Matter soluble in water, %	0.48	0.33	0.21	0.25	0.19	0.48	0.51	0.42	0.53
7	Matter soluble in 0.25 M HCl, %	1.23	0.98	0.85	1.04	0.80	1.15	1.18	1.33	1.56
8	Bulk density, g mL-1	0.27	0.28	0.29	0.35	0.42	0.30	0.37	0.38	0.33
9	Specific Gravity	1.24	1.46	1.56	1.65	1.87	1.43	1.10	1.05	0.88
10	Porosity, %	78.2	74.5	80.2	81.3	75.1	79.0	66.4	63.8	27.1
11	Methylene Blue Number, mg g-1	450	255	195	165	525	150	115	375	154
12	Iodine Number, mg g-1	977	107	1079	1103	1186	1084	1065	1078	1059
13	Fixed Carbon, %	59.1	59.3	62.6	56.5	67.7	57.9	57.8	43.6	57.1
14	Yield, %	52.7	41.2	55.2	56.1	69.2	58.3	57.4	59.5	52.3

Table - 3 Characteristics of effluent samples before and after adsorption

Properties of Samples	Sample 1			Sample 2			Sample 3			Sample 4			Sample 5		
	BA	AA		BA	AA		BA	AA		BA	AA		BA	AA	
		CAC	PPy/ SD		CAC	PPy/S D		CAC	PPy/S D		CAC	PPy/ SD		CAC	PPy/S D
Colour	**Blue**	Nil	Nil	**Maroon**	light red	Nil	**Green**	Nil	Nil	**Yellow**	Nil	Nil	**Violet**	Light Violet	Nil
pH	10.5	7.4	7.1	8.7	6.5	6.8	9.4	7.2	7	8.8	7.3	6.6	10.4	8.5	8.1
Conductivity, µS/cm	9.8	4.3	5.5	11.6	6.2	8.3	14.4	8.5	10.9	10.4	3.3	4.8	16.5	6.3	7.8
TDS, mg/L	6800	3200	3000	4400	2200	2100	18000	11000	9000	5400	3700	2500	21000	13500	10400
Hardness, mg/L	1020	340	320	956	296	224	1223	386	322	835	267	212	1034	310	287
Alkalinity, mg/L	1340	238	206	855	218	188	2011	215	207	1031	182	156	3670	401	395
Chloride, mg/L	745	285	210	985	340	290	1125	350	330	665	235	195	1675	343	284
Sulphate, mg/L	530	245	210	445	225	210	775	320	305	730	255	220	1035	375	310
COD, mg/L	770	320	225	545	210	175	655	325	310	450	215	195	980	365	315
BOD, mg/L	440	30	25	330	50	35	375	40	30	400	40	30	855	65	50
% of colour removal		**86.2**	**94.6**		**78.7**	**83.5**		**89.4**	**95.3**		**90.6**	**97.7**		**72.3**	**80.4**

BA - Before Adsorption
AA - After Adsorption

Bulk density indicates the fibre content present in the precursor material. From the data's shown in Table 2, it is indicated that all the nine carbons have relatively equal bulk density. Methylene blue number is an indication of the ability of a carbon to adsorb high molecular weight substances like dye molecules.

From table 2, CAC5 shows higher methylene blue number greater than 400, which indicates that, the carbon is very effective for the removal of dyes. Iodine number is the most fundamental parameter used to characterize the performance of an activated carbon. It is a measure of the activity level which is often reported in mg/g. It is a measure of micropore content of the activated carbon by adsorption of iodine from solution. It is equivalent to the surface area of carbon between 900 m^2/g and 1100 m^2/g.

From Table 2, it is clear that CAC5 has higher iodine number indicating that it is best suitable for dye removal. In all the processes, the final carbon yield from Table 2 shows encouraging results. CAC5 has higher yield when compared to the yields of all other carbons. This shows that CAC5 is best suited activated carbon of higher porosity which could be very effective in the field of adsorption.

3.2 Adsorption Studies on dyeing industrial effluent

The effluent samples from dyeing industries were collected from the outlet of various dye processing unit immediately after the completion of the dyeing process before discharging the effluent into the common collection tank. The properties of the effluent before and after adsorption with CAC5 and PPy/SD are presented in Table 3.

3.3 Effluent Characteristics

The effluent samples were bright coloured organic compounds and most of them were alkaline in nature. All effluent samples were strongly coloured before treatment but after treatment they became colourless except sample 2 and sample 5. The results presented in Table 3 shows that CAC and PPy/SD reduced all the physico-chemical and biological parameters to a significant level.

The effluent samples 2 and 5 were not completely decolorized by CAC and PPy/SD due to the presence of high organic content present in them which imparts dark colour to the dyes. The organic and inorganic molecules in the dyes compete for the adsorption sites and hence tend to reduce the adsorption capacity of the adsorbents. This may be the reason for the poor adsorption of sample 2 and sample 5 showing removal percentages as 78.7% for CAC and 83.5% for PPy/SD and 72.3% for CAC and 80.4% for PPy/SD respectively. Generally the dark colored dyes such as violet, red and black dyes are very hesitant for the adsorptive removal.

The conductivity of all the effluent samples was decreased to a considerable extent by the two adsorbents. TDS content in wastewater is a measure of salinity. Dissolved salts like carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, calcium, magnesium, iron, and manganese may be some salts present that increase the TDS level in wastewater [14]. High TDS level was observed for the samples 2 and 5 even after treatment. But the remaining samples 1, 3 and 4 showed a very low level of TDS after adsorption treatment.

Hardness of water is not a pollution parameter but indicates water quality, mainly in terms of Ca^{2+} and Mg^{2+}, expressed as $CaCO_3$. Hardness may vary from sample to sample and from place to place [15]. The effluent samples contained high level of hardness before treatment but after the adsorption by adsorbents, the hardness was reduced below 600 mg/L, which is the permissible limit given by BIS standard for wastewater discharge into receiving water bodies.

pH is the measure of acidity or alkalinity of water. It is considered to be the main factor because the quality of an effluent can be decided by its pH value. The pH of all the effluent samples was more alkaline in nature before treatment. After the adsorption of effluent samples by CAC and PPy/SD, the pH values were lying in the range of 6.5 to 8.5 which comes under the desirable pH range of drinking water prescribed by ISI and WHO [16].

Appreciable amount of chlorides, sulphates and alkalinity are removed by the adsorbents namely CAC and PPy/SD and is evident from the results shown in Table 3. BOD is an important index which gives a measure of sewage strength. Usually all the naturally occurring organic molecules and many synthetic compounds can be degraded by microbial activity in the presence of oxygen. The collected effluent samples show very low BOD values after treatment with the adsorbents with the reduction of foul smell which implies that these samples could also be used after treatment for irrigation purposes.

COD is used for determining the organic load of a water body. It is a rapidly measurable parameter for stream and industrial waste studies and control of water treatment plants. High COD levels indicate the toxic condition and the presence of biologically resistant organic substances. The COD values for the samples are reduced after treatment to a significant level. Thus both BOD and COD level decreases in accordance with colour removal of all the effluent samples and is reduced after treatment with CAC and PPy/SD adsorbents.

Thus the treated effluent samples 1, 3 and 4 are completely colourless whereas samples 2 and 5 showed partial colour removal capacity. All the parameters such as pH, TDS, hardness, alkalinity, chlorides, sulphates, BOD and COD were very much reduced by the adsorbents CAC and PPy/SD. Hence these adsorbents could be considered as an efficient and excellent adsorbent for the removal of dyes from wastewater without any neutralization of the effluent.

CONCLUSION

From the results of the present investigation, it can be concluded that,

i) Activated carbon and polypyrrole coated sawdust can be conveniently and economically prepared from casuarina wood.

ii) The extensive characterization studies of different varieties of activated carbon reveal that the phosphoric acid impregnated carbon can be assessed as superior grade carbon.
iii)The colour removal efficiency of low cost adsorbents prepared from casuarina and polypyrrole coated sawdust were used effectively used for the removal of pollutants from industrial wastewater.
iv)From the experimental finding it has been observed that activated carbon and polymer coated saw dust can be used as an effective adsorbent material for the successful removal of color, pH, electrical conductivity, dissolved oxygen, BOD,COD, hardness, alkalinity and TDS from industrial effluent.

On comparing the results, it is obvious that, for the removal of pollutant from effluent water, polypyrrole coated sawdust is an efficient, economic and alternative biomaterial than activated carbon.

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