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Adsorption Studies of the Sugar Phenolic Acids onto Activated Corn Cob Powder (ACCP)

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ABSTRACT

In the present study, the porous adsorbent materials from agricultural waste corn cob were manufactured by using the chemical activation method. The utilization of corn cobs powder for the removal of sugar phenolic acids from there aqueous solution is investigated by batch mode technique. The activated adsorbent material (ACCP) was studied by examining their physical characterizations such as BET surface area, total pore volume, apparent (bulk) density and hardness. The pore distribution falls between macroporous and mesoporous domains. The parameters studied include the contact time, concentration, temperature, pH, dose and concentration of added salts. The optimum conditions observed of maximum adsorption of sugar phenolic acids are near neutral pH. The adsorption process was found to be exothermic as adsorption decreased with increasing temperature. The experimental results show that activated adsorbent materials prepared from agricultural waste corn cob is used as a new kind of decolorizing agent in sugar refining. Very low cost, highly efficient and no need for regeneration are the main characteristics of the product.

***Keywords* – ACPP, Adsorption, Phenolic acids, Sugar color.**

INTRODUCTION

Corn cob is a lignocelluloses material composing of cellulose, hemicellulose and lignin [1] thus by carbonizing the precursor a porous carbon adsorbent would be obtained [2]. Several researchers have reported developing activated carbon from corn cobs, but the surface areas were relatively low and the physical adsorption more energy demanding. Different values of surface areas were reported some of which are a value of 437 m^2/g [3], 664, 850, and 700 m^2/g [4], 608 and 897 m^2/g [5], depending on the carbonization. The removal of color from aqueous solution has been investigated by various physical and chemicals methods [6] such as adsorption, membrane filtration, chemical oxidation etc. Adorption method for color removal using commercial activated carbon is not economical, hence the utilization of efficient cost-effective adsorbents [7] like sugarcane bagasse, corn cobs, peanut shell, wheat straw, barley straw, rice straw, rice hulls etc., are now used in industrial level. The activation of the raw material was accomplished by two basic processes, of which there are many modifications depending upon the starting material and the final product desired. The two basic processes are:

1. Activation through chemical, which is a process depending upon the action of inorganic chemical compounds either naturally present or added to the raw material to degrade or dehydrate the organic molecules during carbonization or calcinations [9].

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2. Activation in the presence of steam, which is a process depending upon selective oxidation of the carbonaceous matter with air at low temperature or steam or carbon dioxide at high temperature.

The color in a raw sugar comes from the phenolics and flavonoids amounting to approximately to two third of it. The phenolic compounds are oxidized, in the presence of phenol oxidase [10] quinones (red color); subsequently producing indole polymers and / or melanin. Anthocyanins decomposes at pH > 8 [11], red in acidic media, become blue and lose color with increasing pH value. In fact, polyphenols are considered as the whole realm of color formation (7-10%) during sugar processing [12]. The color is also formed by the alkaline degradation products (ADP) of hexoses [13]. In addition to this, moisture and iron also contributes to the color [14]. The complex origins, therefore, of color have made it very difficult to develop a single, widely applicable, decolorization system.

In this study, we report H_2SO_4 activation of corn cob to produce activated corn cob powder (ACCP). The adsorbent is relatively common, cheap and abundantly available. The corn cobs powder was directly unable to adsorb the sugar colorants. The physical and chemical properties of corn cobs powder (CCP) are tabulated in Table 1 [15-16].

Table 1. Physical and chemical properties of CCP

Properties	Average	Standard Deviation	Coefficient of Variation (%)
Physical			
Ash content (%)	2.33	0.06	2.62
Volatile (%)	86.89	1.01	1.16
Moisture content (%)	10.78	0.278	2.58
Chemical			
Magnesium (mg/g)	54.40	0.30	0.33
Aluminum (mg/g)	0.01	0.00	0.00
Solubility in water (%)	0.52	0.03	6.56
Solubility in 0.25 M HCI (%)	4.56	0.98	21.49
Calcium (mg/g)	1.70	0.10	5.88
Iron (mg/g)	131.00	2.40	1.83

Maize Production Trends in India (Source: Directorate of Economics and Statistics, Ministry of Agriculture, Government of India)

Production of cereals other than rice and wheat stagnated during the 1980s and declined marginally during the 1990s. During these two decades, maize performed better than other important coarse cereals (barley, sorghum, and pearl millet). Figure 1 shows the maize production in India from 1961 to 2011.

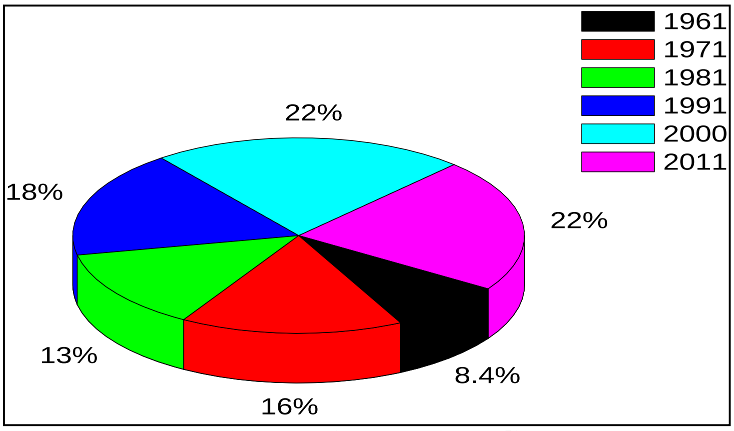

Fig 1: Maize area in India (1961/2011).

MATERIALS AND METHODS

It is worth mentioning here that about 11.5 million tons maize is produced in our country annually. Therefore, the corn cobs is easily available free of cost. Phenolic acids were purchased from Sigma Aldrich. The Studied Phenolics acids are: Chlorogenic acid, p- coumaric acid, p-hydroxybenzoic acid, 7-hydroxycoumarin and Syringic acid. The NaCl (AR), Na_2SO_4 (AR), Na_3PO_4 (AR), $CaCl_2$ (AR), $FeCl_3$ (AR), HCl (AR), NaOH (AR), Na_2CO_3 and H_2SO_4 (AR) are purchased from Sd-fine Chemicals. A new kind of adsorbent is derived from an inexpensive and abundantly available source.

Preparation of Activated Corn Cobs Powder (ACCP)

The corn cobs, which has been used as the sorbent in this study was obtained from local agricultural field (after grains being removed) and the waste cob alone was cut into pieces and crushed. It was washed with double distilled water and oven dried at 110°C overnight. Twenty grams of corncobs are activated by refluxing with 120 ml of 20% H_2SO_4 at 70°C for 5 hr in a round-bottom flask. The slurry was cooled in air and filtered through a glass wool. The filter cake was repeatedly washed with hot double distilled water until the filtrate was neutral and dried at 100-110^0 C. The material was grounded and sieved to desired particles size. Finally, granules of ACCP thus obtained were stored in separate vacuum desiccators until required.

Methodology for Determination of Phenolic Acids

Stock solutions of phenolic acids (10mg/L) were prepared by dissolving appropriate amounts. Standard solutions were prepared by further dilution of stock solutions. The standard tests solutions (100 ml) of afore mentioned phenolic acids were taken in Erlenmeyer flask (200 ml) and pH was maintained using HCl. To these solutions, 1 g ACCP was added and solutions were shacked and filtered. The absorbance of this solution was determined at λ_{max}736 nm. The residual phenolic acid concentration was measured (λ_{max}=736 nm) using standard curve.

Adsorption Studies

Equilibrium adsorption isotherms for the ACCP were determined at 300-rpm at room temperature and different concentrations of phenolic acids. On the basis of the experimental data obtained with the ACCP for phenolic acids, the quantities of the adsorbed phenolic acids were calculated. Thus, we have calculated the adsorption capacity, q_e (mg/g) with the relation below:

$$q_e = \frac{(C_i - C_f)\,V}{m}$$

where C_i, C_f are the initial concentration of solute and final concentration of solute respectively; V is the volume of solution taken and m is the mass of the adsorbent used in experiment.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

The FT-IR spectra of ACCP were scanned in between 400-4400 cm^{-1} and are shown in Figure 2. Some of the bands originating from the sample are characteristics of -OH stretching (3454 cm^{-1}). The peak at 1300-1650 cm^{-1} was observed due to the stretching vibration of N-H.

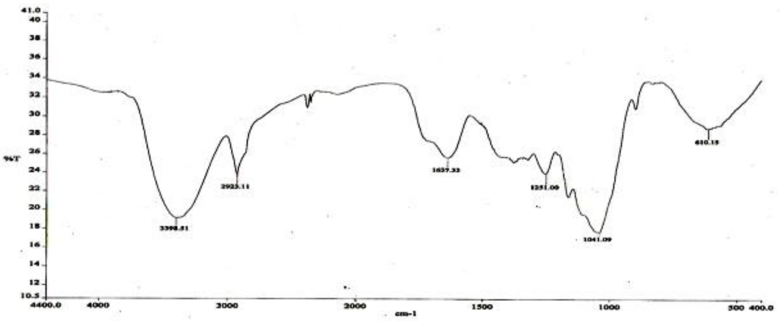

Fig 2: FT-IR spectrum of ACCP (30-60 mesh size).

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SEM Characterization

The SEM pictures shown in Figure 3 clearly demonstrate the enhanced porosity in activated corn cobs powder and alumina treated corn cobs powder.

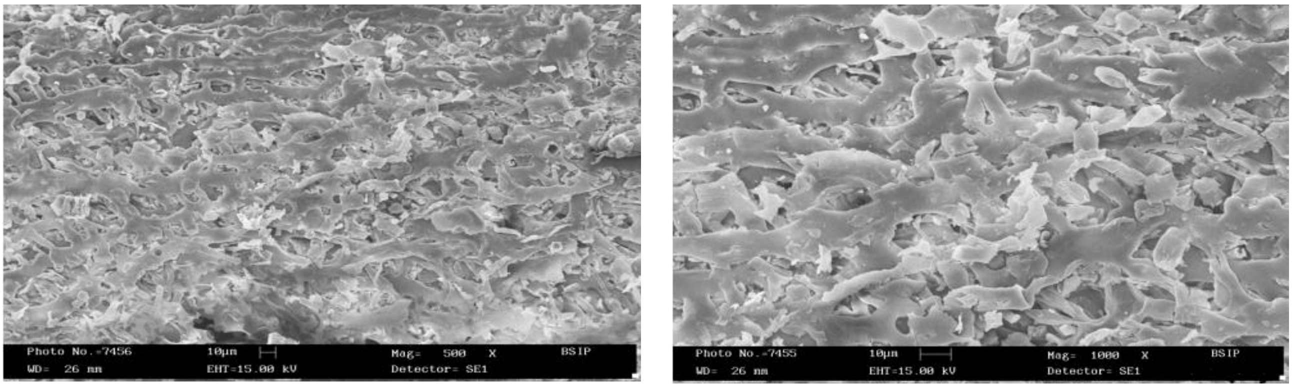

Fig 3: SEM pictures of activated corncobs powder (ACCP) at 500X and 1000X.

Physical and Chemical Characteristics of ACCP

The physical appearance of the product derived from CCP looks like light yellow amorphous solid. The physico-chemical properties of ACCP are tabulated in Table 2.

Table 2. Physical and Chemical Properties of ACCP

Specific Surface Area (S_{BET}) m^2g^{-1}	Pore Volume cm^3/g	Bulk Density (g/ml)	Hardness	Conductivity (µS)	pH	Ash content (% dry weight)
1.34	0.0063	0.31 ± 0.01	73.22 ± 0.6	74 ± 10	6.35 ± 0.06	2.75 ± 0.07

Elemental Characterization

The elemental analysis of ACCP shows the different chemical contents as given below Table 3.

Table 3. Elemental Analysis of ACCP

Element	% Composition	
	Present work	Literature data [17]
Carbon	44.34	44.66
Hydrogen	7.17	6.04
Nitrogen	1.51	0.2
Ash	0.5	-

Effect of Initial Concentration of Phenolic Acids

The adsorption process is highly dependent on concentration of the phenolic acids. The equilibrium sortion capacities of the sorbents obtained from experimental data at different initial phenolic acids concentration are presented in Figure 4. The adsorption capacity of phenolic acids on the surface of ACCP it's in the range of 0.35mg/g to 0.64 mg/g.

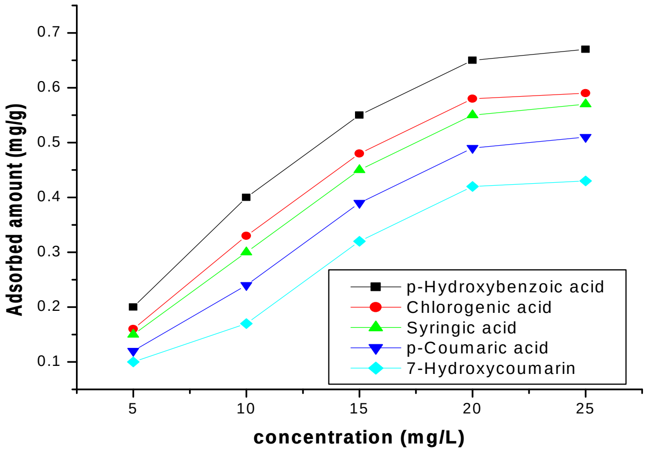

Fig 4: Adsorption isotherm of phenolic acids onto ACCP at different concentration (pH= 6.5, temp. = 25±0.5°C, shacking time = 5h (200 rpm), mesh size = 100, dosage = 1 g/100 ml.

Effect of Contact Time

The adsorption data for the uptake of phenolic acids versus contact time at constant initial concentrations is presented in Figure 5. The results showed that equilibrium time required for the adsorption of phenolic acids on ACCP was almost 4.5h. However, for subsequent experiments, the samples were left for 5h to ensure equilibrium. The higher sorption rate at the initial period (first 120min) may be due to an increased number of vacant sites on the adsorbent available at the initial stage, as a result there exist increased concentration gradients between adsorbate in solution and adsorbate on adsorbent surface.

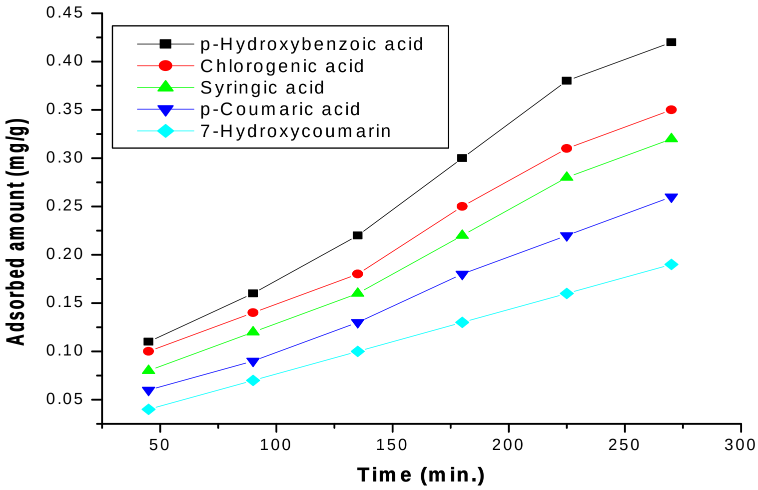

Fig 5: Adsorption isotherm of phenolic acids onto ACCP at different contact time (pH =6.5, temp. = 25±0.5°C, mesh size = 100, concentration=10mg/L, adsorbent dosage = 1g/100ml).

Effect of Adsorbent Dosage

The effect of ACCP mass on the amount of removal of phenolic acids was obtained by contacting 100 ml of each phenolic acid solution of initial concentration of 10mg/L with different weighed amount (0.5, 0.75, 1.0, 1.25, and 1.5 g) of ACCP separately in stopper conical flask. Figure 6 shows the effect of adsorbent dosage on the removal of phenolic acids. The percentage removal of phenolic acids increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage.

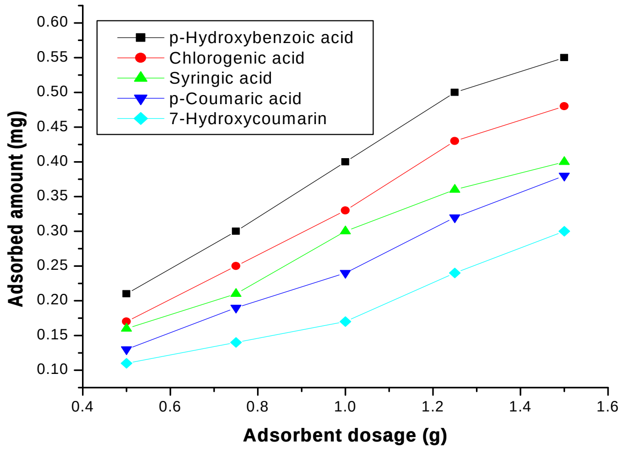

Fig 6: Adsorption of phenolic acids onto ACCP at different adsorbent dosage (pH = 6.5, temp. = 25±0.5ºC, shacking time = 5h (200 rpm), mesh size = 100, concentration = 10mg/L).

Effect of pH

The effect of pH on the amount of phenolic acids removal was analyzed over the pH range from 2 to 12. In this study, 100 ml of phenolic acid solution of initial concentration of 10mg/L for phenolic acid was taken in stoppered plastic conical flask. Each sample was then shacked for 5h at a constant rpm (200) using water-bath shaker (Model-YSI-413-EX) at 27 ± 0.2 ^{0}C. All the pH measurements were performed using Toshcon pH meter ((Model NO. CL 46 +, Toshcon, India). Figure 7 shows the effect of pH on the removal of phenolic acids on the surface of ACCP.

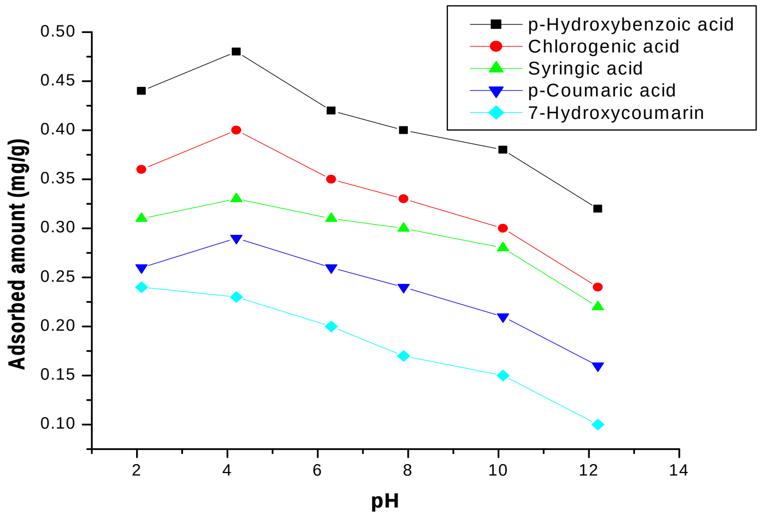

Fig 7: Adsorption isotherm of phenolic acids onto ACCP at different pH values (temp. = 25±0.5ºC, shacking time = 5h (200 rpm), mesh size = 100, adsorbent dosage = 1 g/100 ml).

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. Figure 7 illustrates the effect of pH on the adsorption of phenolic acids onto ACCP. It was observed that the uptake of phenolic acids by ACCP was almost constant in the pH range of 10-6.5. At low pH values, the surface of the ACCP would be protonated and resulted in a stronger attraction for negatively charge phenolate ions because phenols, being weakly acidic, partially ionizes in solution.

Effect of Temperature (Thermodynamic Study)

The effect of temperature on adsorption of phenolic acids on ACCP was studied over a temperature range of 30-50^0 C. The adsorption of phenolic acids onto ACCP was found to decrease with increase in temperature. Hence, the adsorption is exothermic in nature. It may be due to a relative increase in escaping tendency of the phenolic acids from the solid phase to bulk phase with increase in temperature of the solution [18]. Figure 8 illustrates the effect of temperature on the adsorption of phenolic acids onto ACCP.

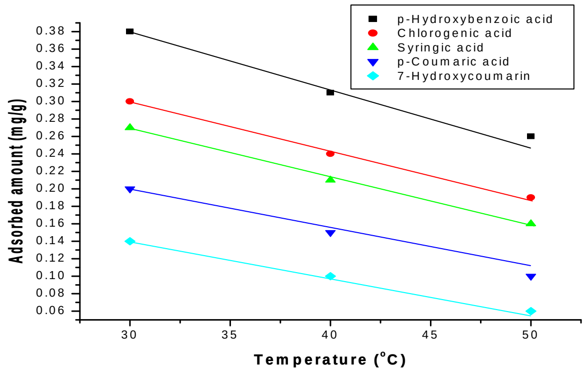

Fig 8: Adsorption isotherm of phenolic acids onto ACCP at different temperature (pH = 6.5, shacking time = 5h, mesh size = 100, dosage = 1 g/100 ml, concentration = 10mg/L).

Effect of Ionic Strength

In the present study, the influence of the addition of salts (ionic strength) on the amount and rate of the adsorption was investigated by adding different salts of the concentration range 0.02-0.1M. The results are shown in Figure 9-10 and they clearly demonstrate and adsorption of phenolic acids increases with increasing salt concentration and obeys the sequence; $Cl^- < SO_4^{2-} < PO_4^{3-}$. Similarly, the cations were added in the same concentration range as anions and the effectiveness was found to obey the sequence; $Na^+ < Ca^{2+} < Fe^{3+}$. Salts when added to an adsorption system often respond via the two mechanism; viz. either by the screening of charges in the solution or by the preferential (selective) adsorption of added ion to the surface.

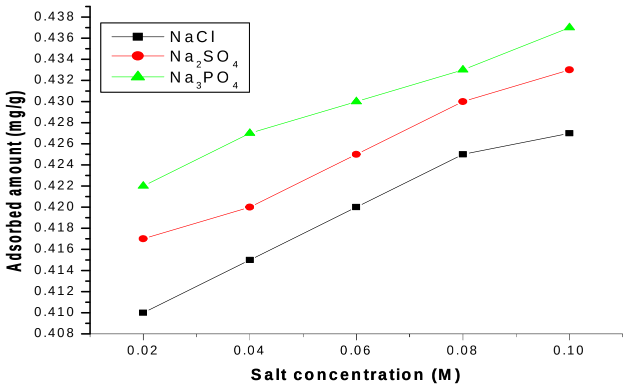

Fig 9: Influence of ionic strength (anions) on adsorption of p- hydroxybenzoic acid onto ACCP (pH = 6.5, temp. = 25±0.5ºC, shacking time = 5h, mesh size = 100)

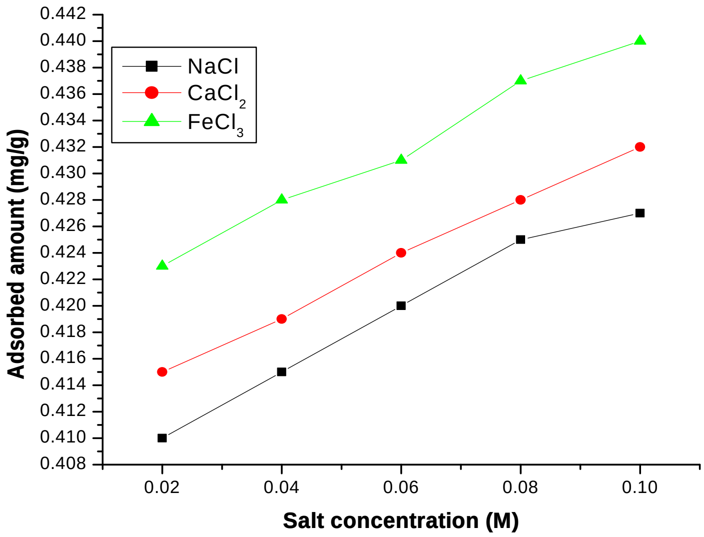

Fig 10: Influence of ionic strength (cations) on adsorption of p- hydroxybenzoic acid onto ACCP (pH = 6.5, temp. = 25±0.5°C, shacking time = 5h (200 rpm), mesh size = 100)

CONCLUSION

The activated corn cobs powder was found to be very efficient, instantaneous and economical for removing phenolic acids from aqueous solution. The adsorption of phenolic acids increases with increasing salt concentration suggesting electrostatic adsorption. The adsorption was found to be exothermic in nature. The raw materials employed for preparation of the substrate are cheap and easily available. Thus, it can be concluded that ACCP seems to offer a very cheap, efficient and useful adsorbent material for removal of sugar phenolic acids. The studies revealed that activated corn cobs proved to be a good low-cost adsorbent.

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