DEVELOPMENT OF ACTIVATED CARBON FROM COMBINED PLASTIC WASTE FOR TREATING INDUSTRIAL PULP AND PAPER MILL EFFLUENT

VIPUL GUPTA,[*] NISHI K. BHARDWAJ[*] and RAVINDRA K. RAWAL[**]

[*]*Avantha Centre for Industrial Research and Development, Thapar Technology Campus, Patiala – 147 004, India*
[**]*Department of Chemistry, Maharishi Markandeshwar Deemed to be University, Mullana – 133 203, India*
✉ *Corresponding author: Nishi Kant Bhardwaj, nishi.bhardwaj@pt.iitr.ac.in*

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An adsorbent was prepared from combined plastic waste and characterized in comparison with commercial adsorbents. The adsorption study was carried out for elimination of lignin and colour from the E_{OP} stream of a paper mill effluent by using activated carbon in 100 mL batch experiments. Langmuir and Freundlich isotherm models were employed to analyze the adsorption isotherms and it was found that the Freundlich model could fit the data better than the Langmuir model. The value of constant 'n' was found to be >1, indicating the nature of adsorption is physical. The R_L value (<1) confirmed the favorability of the adsorption process. The removal efficiency of the developed adsorbent (AC-CPW) was found to be 82.7 ± 1.32% for lignin, and 94.5 ± 2.71% for colour, at 10 g/100 mL adsorbent dose. The results demonstrate that abundant plastic waste can be turned into an adsorbent to be used for removal of pollutants from highly contaminated E_{OP} stream of paper mill effluents.

Keywords: activated carbon, Freundlich isotherm, Langmuir isotherm, plastic waste material, wastewater

INTRODUCTION

Because of exhausting fossil fuel resources, the ever-growing energy demand and significant pollution, the management of waste plastic and the treatment of wastewater are major challenges that urgently need solutions.

The pulp and paper industry is among the fastest growing sectors in India and it depends on a variety of raw materials and plenty of water for its further expansion to satisfy the need and demands of the people.[1] Thus, the paper and pulp industry, alongside tannery, textile and electroplating industries, is the largest consumer of water and produce extremely polluted wastewater in almost equivalent quantities to fresh water consumption.[2] The paper industry is categorized as one of the largest polluting industries and the chief contributor of pollution load to aquatic bodies. The mills manufacturing pulp and paper generate diverse volumes (about 60-125 and 10-50 m^3) of wastewater per ton of paper production on the basis of the type of raw material used.[3]

Amongst the different processes carried out in pulp and paper mills, the pulping and bleaching processes produce wastewater with high concentrations of toxic pollutants and significantly loaded with suspended solids, with biological and chemical oxygen demands, chlorinated compounds and recalcitrant organic compounds. The pulping process type and the bleaching sequence affect the toxicity level of the effluent from the bleach plant.[4] Colour is easily recognized due to its aesthetical value, thus having become the fundamental problem of the pulp and paper industry. Organic components, mainly extractives of wood, synthetic dyes, tannins and lignin are responsible for colour, but especially lignin and its derivatives containing colour-contributing chromophoric groups are the real culprit.[5,6] Lignin is complex in nature and cannot be represented by a single structure, as it varies as a function of plant species, place of growth *etc*. Being a complex phenolic component, it is difficult to remove. The presence of the colour-contributing organic compounds increases

the BOD, which reduces the intensity of dissolved oxygen and also trims down the sun light penetration to water bodies, which are essential for survival of aquatic life.[7] As the untreated effluent is toxic to aquatic life, it is essential to remove pollutants from wastewater before it can be discharged into water bodies.

The wastewater from pulp and paper mills is characterized mainly by its pH, total dissolved solids, total suspended solids, chemical oxygen demand, biochemical oxygen demand, colour, odour, sodium absorption ratio and adsorbable organic halogens.[8] Various wastewater management practices have been suggested to decrease the aforementioned pollutants as these put pressure on paper mills.[9] At the moment, common wastewater treatment processes include sedimentation, coagulation/flocculation, activated sludge process, oxidation process, anaerobic treatment process and membrane filtration.[10] These processes have high operational or maintenance costs, are time-consuming and require trained manpower. Also, conventional chemical and biological methods used for removal of colour and lignin are not very efficient.

Today, there is a gradually growing demand for plastic materials in everyday goods, which however, generates huge amounts of plastic waste, further increasing the pollution load on the environment.[11] From the global average of 28 kg at the moment, the mean per capita utilization of plastic goods in India is close to 11 kg, and expected to grow to about 20 kg by 2022, as per the estimation of the Ministry of Petroleum and Natural Gas (Government of India).[12] Normally, the 'use and throw' strategy is in practice among the majority of people because plastic goods are low cost. This is the main reason why, in many countries, the major part of plastic waste is accumulated in landfills and not recycled. The major component of polymeric plastic is carbon, which remains in the environment for a long time, because of its non-degradable nature. Moreover, because of their light weight and stability, plastics are easily transported by the wind to forests and aquatic bodies, being a real environmental threat.[13]

To overcome the complexity associated with the management of plastic waste, methods to convert waste plastic into value-added products are urgently required. Pyrolysis is the foremost method to shrink the huge amount of polymer wastes and save a huge amount of energy.[14] Pyrolysis converts the plastic polymer macromolecules into solid, gaseous and liquid material, by fragmenting them using a particularly designed reactor at different temperatures (400-1000 °C).[15] Catalysts are used to improve the pyrolysis process of plastic waste and to augment process efficiency by increasing the yield of volatiles.[16] The active role of the catalyst in the pyrolysis process motivated the researchers to study a range of catalysts alone and their combination for the smooth pyrolysis of polymeric materials, as well as to enhance the quality of recovered products. Alongside fuels, other important products could be obtained, like hydrogen, solid char, chemicals, olefin-rich fractions *etc*.[17] The residual char having a high percentage of carbon also results from the pyrolysis process. This carbon can be a good forerunner for the manufacture of carbon black, along with other products, which can be further transformed into activated carbon.[18]

So far, the adsorption process is considered as one of the best techniques for the removal of colour and other pollutants from aqueous media.[19] The adsorption of toluene using honeycomb as adsorbent under high temperature and humidity conditions was reported earlier.[20] Another study demonstrated the adsorption of para-nitrophenol and phenol from aqueous solutions using magnetic activated carbon, which was synthesized from cauliflower waste.[21] Activated carbon (AC), with its high surface area, is usually hydrophobic and capable of removing colored or recalcitrant organic compounds from wastewater, which could not be removed by other treatments. The effectiveness of AC has been confirmed for the treatment of wastewaters from paper mills in various studies.[22-24] The adsorption of colouring materials, such as dyes and chromophoric compounds, organic pollutants and metal ions from wastewaters was achieved using AC from cellulosic materials.[25] The efficacy and adaptability of AC has been reported in the elimination of various pollutants, such as colour,[26] COD,[27] BOD,[28] along with various heavy metals[29] from effluents.

Although the literature supports the conversion of plastic waste to valuable products, such as oil, char and gases, its exploitation for producing adsorbents for the treatment of wastewater and similar applications is scarcely reported. Earlier, our research group investigated the preparation of AC from waste plastic and its application for the removal of pollutants from pulp and paper mill

composite wastewater (inlet to effluent treatment plant, coming from different sections of the paper mill), using the central composite design (CCD), with a view to optimize conditions.[30] There is very limited literature available on the preparation of highly efficient AC from plastic waste and its utilization for the removal of pollutants of pulp and paper mill wastewater. Wastewater from the pulp and paper mills comprises of a broad range of substances, organic and inorganic. Wastewater generated during the bleaching of pulp is accountable for most of the organic matter, colour and toxicity in the effluent. The novelty associated with this research paper resides in the preparation of AC from combined plastic wastes and comparing the efficiency of the prepared AC with that of two commercially available products. For this, the effect of different parameters, such as adsorbent dosage, temperature, agitation rate, contact time and pH, on the adsorption process, to eliminate colour and lignin from extremely polluted E_{OP} stream generated by a pulp and paper mill, was studied. This research also considers the Langmuir and Freundlich isotherm models to study the adsorption isotherms for the process.

EXPERIMENTAL

Materials

Waste plastic materials, including polystyrene – PS, polyethylene – PE, polypropylene – PP, and others, were collected as plastic goods, according to recycling symbols mentioned on the label. The collected plastics mainly consisted in plastic bags, shampoo bottles, detergent bottles, plastic furniture, toys, automobile parts, PLA packages *etc*., which were gathered locally from houses, shops, factories and the solid waste management facility of the Yamunanagar-Jagadhri Municipal Corporation.

Combined plastic waste material (CPWM) was utilized for the study. Batches of 60 g of plastic wastes, containing three main types of plastics, namely PE 30 g, PP 15 g and PS 15 g, were used for pyrolysis. The plastic material was firstly washed to remove dirt particles, air dried and then cut into small 2.5-5 cm pieces.

Chemicals, such as HCl, $ZnCl_2$ and others used in the study were procured from Fisher Scientific. Two commercial ACs were obtained from Loba Chemie and Fisher Scientific for comparison purposes, and denoted as AC-LC and AC-FC, respectively. The effluent from the alkali extraction (E_{OP}) stage from the pulp bleaching section of a kraft paper mill in Haryana utilizing mixed hardwoods and bamboo raw materials for producing writing/printing paper was used in the current study. The mill followed the $C_DE_{OP}D_1D_2$ bleaching sequence (mixed chlorine and dioxide represented as C_D, alkaline extraction using oxygen and peroxide represented as E_{OP} and chlorine dioxide stages represented as D_1 and D_2) to produce bleached pulp of 88-89% ISO brightness.

Activated carbon preparation

A two-step process was applied to convert CPWM to activated carbon. In the first process, the CPWM was heated in the pyrolysis chamber to about 500 °C under nitrogen gas with a heating rate of about 10 °C/min for 1 h to obtain the char remainder (CR). In the next step, the CR was converted to activated material using impregnation with zinc chloride ($ZnCl_2$) as activator, at activator to char mass ratio of 3:1, 850 °C temperature, and retention time of 2 h. After carbonization, the resultant carbon material was saturated with 3 M HCl to unwrap cavities of carbon material and to get the spongy arrangement. Subsequently, rinsing with distilled water was used to wipe out the remaining HCl from the carbonized carbon material before drying the material at 103-105 °C in an oven to obtain porous combined plastic waste activated carbon (AC-CPW). This AC-CPW sample was ground and sieve on a 212 micron IS mesh, then weighed and stored in a sealed bottle.

Activated carbon characterization

The ash, moisture, fixed carbon and volatile matter of AC-CPW, along with AC-LC and AC-FC samples, were determined as per Indian standard IS: 1350 (part 1). The CHNS (carbon, hydrogen, nitrogen and sulfur) were analyzed by an organic elemental analyzer (Perkin Elmer, Series II CHNSO). An ELICO pH meter was used to measure the pH according to IS: 877. The bulk density was determined by using ASTM D2854-70 as standard procedure. The bomb calorimeter method was used to determine the gross colorific value (GCV) as per IS: 1350 (part 2).

The surface morphology and porosity of the samples were analyzed by SEM (JEOL JSM-6510 LV) at 15 kV accelerating voltage. The standard procedure was used to prepare the samples, which were scanned at different magnification (500X, 1,000X and 2,000X). A Perkin Elmer spectrophotometer (USA, Frontier-104287), provided with the ATR accessory, was used to record the FTIR spectra of the samples in the wavenumber range between 4,000 and 400 cm^{-1}.

The adsorptive efficiency of activated carbon samples under the influence of their adsorption characteristics was analyzed by iodine (IN) and methylene blue (MB) numbers. The MB number facilitates finding out the mesopores value (size between 20-50 A^0) of AC, while microporosity (size 0 to 20 A^0, or up to 2 nm) of AC is found using IN. MB and IN numbers were measured by following the methods described earlier.[30] The specific surface area (SSA) of the combined plastic waste derived activated carbon and the other two commercial activated carbons

was calculated using the measured IN and MB numbers, by Equation (1):

$$\text{Specific surface area, } m^2/g = 228 - 0.101\times MB + 0.3\times IN + 1.05\times10^{-4}\times MB^2 + 2.0\times 0^{-4}\times IN^2 + 9.38\times10^{-4}\times MB\times IN \quad (1)$$

where the MB value is the methylene blue number (mg/g), and IN value is the iodine number (mg/g) of carbon sample.

Wastewater stream characterization

After collection of E_{OP} stage wastewater, it was analyzed for different physico-chemical parameters, including lignin, colour, TDS, TSS, BOD, COD, pH, AOX and SAR using the corresponding standard methods, as detailed in Table 2. The effluent was preserved at 4 °C to avoid degradation until its use in the experiments. The experiments were conducted in triplicate at each condition and average values were reported with an uncertainty range at 95% confidence level.

Batch adsorption trials

The effects of different variables, including pH, adsorbent dose, agitation rate, contact time and temperature, were observed by conducting batch type adsorption experiments with 100 mL of E_{OP} stage wastewater. These variables were varied as follows: pH in the range of 5 to 12, adsorbent dose: 1.0 to 15 g, agitation rate: 50 to 175 rpm, contact time: 0.5 to 10 h, and temperature: 20 to 45 °C. The variables were observed one at a time, while the others were kept constant.

Once the predetermined time period for the adsorption process was over, the ACs were removed from the effluent by the filtration assembly using Whatman no. 1 filter paper, and the filtrate was analyzed for residual colour and lignin content using a UV/Vis spectrophotometer at 465 nm and 280 nm, respectively, and the percentage removal efficiency was obtained using Equation (2):

$$\text{Removal efficiency, \%} = \frac{(Ci - Ce)}{Ci}\times 100 \quad (2)$$

where Ci and Ce are the initial and final concentration after a definite time period of adsorption, respectively.

Mathematical modeling

For a better explanation of the adsorption process at equilibrium, the adsorption isotherm is appropriate for describing the interactions between the solid phase of the adsorbent and the liquid phase of adsorbate molecules.[20] In this study, the interaction of ACs as solid phase with pollutants of E_{OP} stream as liquid phase was discussed by means of Langmuir and Freundlich isotherms.

The Langmuir isotherm implies monolayer adsorption on the adsorbent surface with consistent binding sites.[31] Once the binding sites are occupied, the adsorption process is discontinued and no more addition of adsorbate on the surface of the adsorbent will take place. This situation confirms the saturation point of the adsorption, indicating that the surface attained a point when maximum adsorption would be achieved,[32] which is conveyed by Equation (3):

$$\frac{Ce}{qe} = \frac{1}{q_{max}K} + \frac{C_e}{q_{max}} \quad (3)$$

where Ce symbolizes the equilibrium concentration of lignin (mg/L) and colour (Pt-Co unit) in the wastewater, qe stands for equilibrium adsorption capacity, *i.e.* the extent of pollutant (colour and lignin) of E_{OP} stream adsorbed at equilibrium on the adsorbent surface (mg/g), q_{max} represents the maximum adsorption capacity, *i.e.* the theoretical maximum amount of pollutant that can be adsorbed corresponding to complete coverage of the adsorbent surface by a monolayer of pollutant molecules (mg/g), and K is the Langmuir constant (L/mg) related to the affinity between the adsorbate (pollutant) and the adsorbent (activated carbon). qe is the dependent variable in the Langmuir model and is measured experimentally. Ce reflects the residual concentration of pollutant in wastewater. Plotting 1/qe versus 1/Ce gives a straight line with an intercept of $1/q_{max}$ and a slope of $1/(q_{max}\ K)$, respectively. K is an important factor in calculating the equilibrium parameter (R_L) that helps convey the favorability of the adsorption process. A higher K value suggests a stronger interaction between the pollutant and the activated carbon. R_L is determined by the following Equation (4):

$$R_L = \frac{1}{1 + KC_o} \quad (4)$$

where Co symbolizes the initial pollutant concentration (mg/g). The values of R_L indicate the type of the adsorption process, such as unfavorable (when $R_L > 1$), linear (when $R_L = 1$), favorable (when $0 < R_L < 1$), and irreversible (when $R_L = 0$). R_L helps predict the feasibility and efficiency of adsorption under given conditions.

The Freundlich isotherm is an empirical model, which is not just bound to monolayer adsorption, but also expresses multilayer adsorption during the process and is mathematically represented as Equation (5):

$$\frac{x}{m} = KC^{\frac{1}{n}} \quad (5)$$

where x/m symbolizes the amount of the pollutants of the E_{OP} effluent as adsorbate (x) on the surface of the adsorbent (m), and is expressed in mg/g. C represents the pollutants concentration in the E_{OP} effluent; K is the Freundlich adsorption constant and n is the heterogeneity factor. The logarithmic form of the above equation is represented as Equation (6):

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log C \quad (6)$$

The plot of log x/m *versus* log C would signify a straight line, having a slope of 1/n and an intercept with the value of log K on y axis correspondingly. The n value represents the extent of nonlinearity between the pollutants concentration in the E_{OP} stream and ACs, and helps to observe the nature of the adsorption process (unfavourable, when $n < 1$; linear, when $n = 1$; and favourable, when $n > 1$). A smaller 1/n value (*i.e.*, close to 0) indicates high heterogeneity in adsorption energies, while a value closer to 1 indicates uniformity in adsorption energy across the surface.

RESULTS AND DISCUSSION

Characterization of different ACs

The physical and adsorptive properties of AC-CPW and commercial ACs, such as AC-LC and AC-FC, are presented for comparison in Table 1. The data on proximate analysis disclosed that the ash and moisture contents were very low in comparison with the carbon content in commercial ACs, which implies the materials' effectiveness as fine quality adsorbents.[16] The trend was identical in AC-CPW, as its carbon content was observed to be medium between the values of the two commercial ACs. The ash content in AC-CPW was found to be slightly higher in comparison with that of commercial ACs. The higher ash content indicates the partial removal of the activator from the carbon material during its washing, which impacts its effectiveness for adsorption. The elemental analysis results established the existence of satisfactory carbon content (80%) in AC-CPW, compared to commercial ACs, which was achieved as a result of eliminating the ash content during washing.

The results also confirmed that the gross calorific value (GCV) of the AC-CPW against the commercial ACs was found to be in line with the trend described above. The addition of impregnating materials, together with the plastic char, has a constructive impact, so that the chemically activated AC-CPW has a bulk density (0.23 g/cm^3) similar to those of the commercial ACs. The pH of AC-CPW and both commercial ACs was found in the neutral range.

The adsorption efficiency of all ACs was examined with regard to MB and IN values, and the results disclosed that the MB and IN values of AC-CPW, 188 and 915 mg/g, respectively, were found in between the values of AC-LC and AC-FC. The corresponding data pointed towards the good adsorption capacity of AC-CPW. The specific surface area of AC-CPW, 816 m^2/g, was also found in between the values of AC-LC and AC-FC, which had values of 779 m^2/g and 905 m^2/g, respectively.

The surface morphology micrographs of AC-CPW obtained from pyrolysis of MWP, as well as those of both commercial ACs, are presented in Figure 1. The micrographs revealed an enormous quantity of arbitrarily distributed pores for AC-CPW and commercial ACs. The achieved exterior morphology of AC-CPW is in line with that of commercial ACs, confirming the suitable amount of activator to create infinitesimal cavities.

Table 1
Characteristics of AC-CPW, AC-LC and AC-FC

Parameter	AC-CPW	AC-LC	AC-FC
Moisture, %	0.28	0.52	0.27
Ash, %	5.67	3.14	2.13
V.M., %	10.23	13.53	11.54
F.C., %	83.82	82.99	86.06
C, %	85.71	82.79	90.07
H, %	2.35	1.55	0.93
N, %	0.0	0.0	0.25
S, %	0.11	0.0	0.17
GCV, kcal/kg	8,212	8,125	8,225
Bulk density, g/cm^3	0.23	0.25	0.23
pH	6.94	7.67	7.13
MB value, mg/g	188	180	201
IN value, mg/g	915	878	1,005
Specific surface area, m^2/g	816	779	905

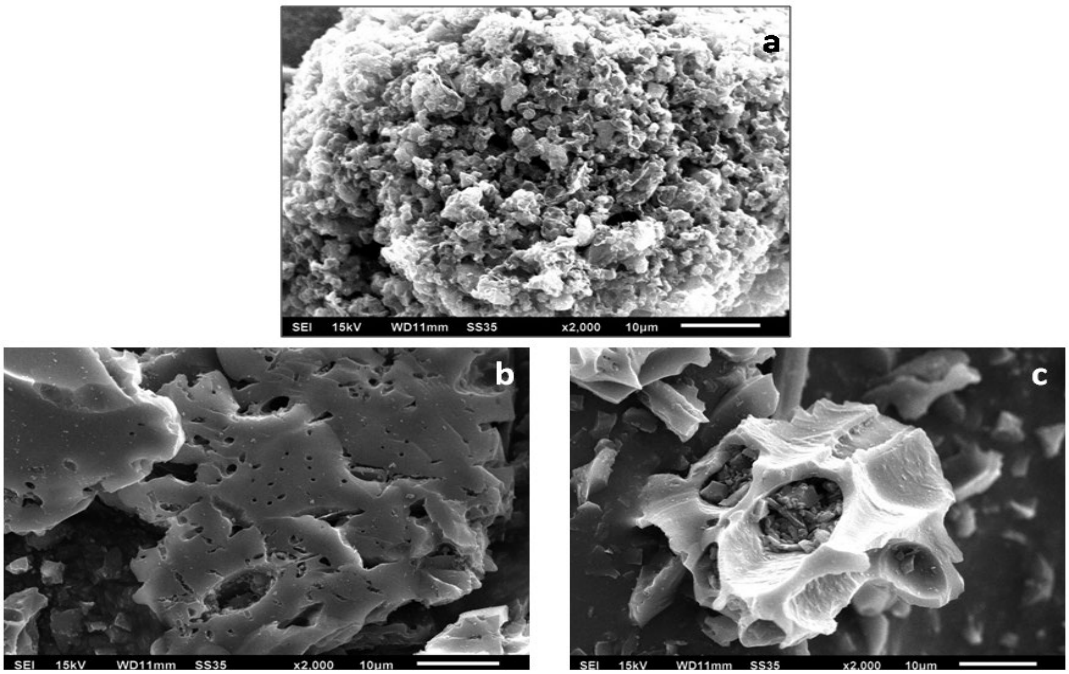

Figure 1: Scanning electron microscopy images: (a) AC-CPW, (b) AC-LC and (c) AC-FC

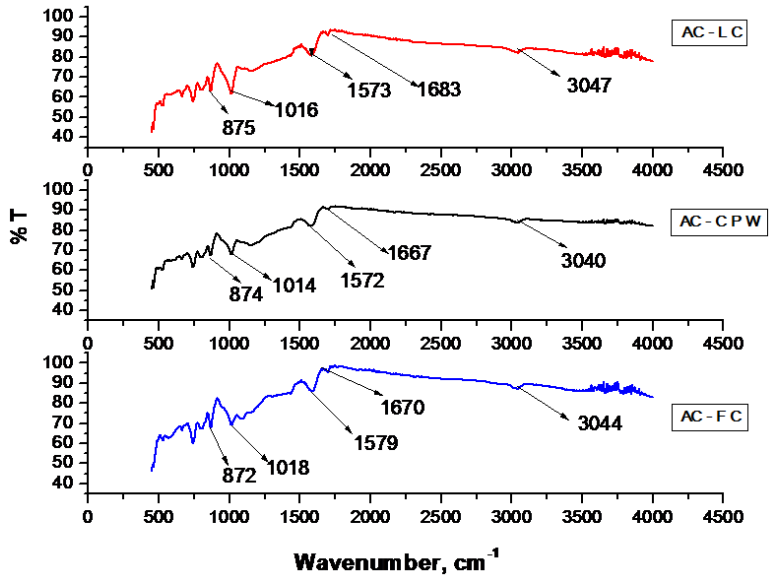

Figure 2: FTIR spectra of AC-CPW, AC-LC and AC-FC

The FTIR-ATR was used to analyze the functional groups and the bonds that may be present in AC-CPW and commercial ACs. As shown in Figure 2, the peak at 3040-3047 cm^{-1} confirmed the existence of =C-H stretch on the exterior of different ACs, the peak in the range of 1667-1683 cm^{-1} specified the presence of carbonyl (C=O) stretching of ketone or aldehyde; the peak in the range 1573-1579 cm^{-1} was due to the aromatic ring C=C stretch and the band at 1014-1018 cm^{-1} indicated alcoholic (R-OH) groups. The peak found at 872-875 cm^{-1} is due to the =C-H bend, confirming the existence of di-substituted *cis* out-of-plane vibration in symmetrical alkenes.[33]

Wastewater stream characterization

The characteristic physico-chemical parameters of the E_{OP} stream are shown in Table 2. The pH of the E_{OP} stream is generally known to be in the range from 10 to 12, and in this study it was 11.10. The lignin and colour of the stream

were measured as 293.4 mg/L and 1,121 Pt-Co unit, respectively. The TDS (total dissolved solids), and TSS (total suspended solids) were 5275 ppm and 49.5 ppm, respectively. The COD and BOD values of the E_{OP} stream were 1018 mg/L and 860 mg/L, respectively. The chlorophenolic content of the E_{OP} stream as measured by AOX was 72.5 mg/L. The sodium adsorption ratio (SAR), a measure of the suitability of water for irrigation purposes for agricultural use was quite high, with a value of 92.8. In general, the water with low SAR values is more suitable.[34]

Table 2
Initial characteristics of E_{OP} stream

Parameter	E_{OP} stream	*UR	Standard method used
pH	11.10	±0.06	IS:3025 P-11
COD, mg/L	1018	±21.3	IS: 3025 (Part 58)
BOD, mg/L	860	±62	IS: 3025 (Part 44)
TSS, mg/L	49.5	±0.9	IS: 3025 (Part 17)
TDS, mg/L	5275	±30	IS: 3025 (Part 16)
AOX, mg/L	72.5	±1.2	ISO: 9562; 2004
SAR	92.8	-	
Na, mg/L	1729	±25.8	APHA Method 3111 B
Ca, mg/L	33.03	±0.5	
Mg, mg/L	1.345	±0.03	
Colour, Pt-Co unit	1121	±22.3	APHA Method 2120 C
Lignin, mg/L	293.4	±5.6	Pearl and Benson, 1940

*UR signifies the uncertainty range of characterization parameter at 95% confidence level

Effect of process variables for the reduction of pollutants

To study the effect of different process variables for eliminating pollutants from the E_{OP} stream of the pulp and paper mill, mainly color and lignin in terms of percent removal efficiency were observed. The major responsible factors, namely ACs dose, temperature, agitation rate (rpm), contact time and pH were investigated and the individual effect of each process variable was examined with regard to the reduction of lignin content and color of the effluent samples.

Adsorbent dose

The effect of adsorbent material dose (AC-CPW, along with both commercial ACs) on the pollutants adsorption from the pulp and paper mill E_{OP} stream was determined as shown in Figure 3 (a). The effect of adsorbents was studied at varying dose levels in the rage of 1.0 to 15.0 g/100 mL, while the rest of the variables were kept stable (pH, temperature, contact time and agitation rate as 11.1, 25 °C, 3 h, and 125 rpm, respectively).

The concentration of lignin and colour of the E_{OP} stream was reduced by up to 87.9 and 95.5%, respectively, after the treatment. The adsorption of pollutants was affected by the adsorbent dose, adsorption efficiency increasing with an increased dose of various adsorbents up to 10.0 g/100 mL and a small increase was further found at 15.0 g/100 mL dose. The adsorption sites of different ACs remain unsaturated throughout the adsorption process, whereas the quantity of vacant sites for adsorption rises by raising the adsorbent dose. The result indicated that the efficiency of AC-CPW as adsorbent was found to be in between of those of the commercial ACs for the treatment of E_{OP}.

Temperature

Adsorption is responsive to the reaction temperature, which affects the efficiency of adsorption of different ACs. In the present study, the effect of adsorbents was studied at varying temperature levels in the range of 20 °C to 45 °C, while the rest of the variables were kept constant (ACs dose, pH, agitation rate and contact time as 10 g/100 mL, 11.1, 125 rpm and 3 h, respectively). As the temperature was enhanced from 20 °C to 35 °C at 10 g/100 mL dose, an increase of about 2.3, 3.3 and 1.9% in lignin removal efficiency and of 3.4, 6.8 and 2.8% in colour removal efficacy was observed for AC-CPW, AC-LC and AC-FC, respectively. The removal efficiency of both pollutants was found to decline with further rise of temperature, *i.e.* up to 45 °C, as shown in Figure 3 (b). The data may

reveal that beyond 35 °C, the adsorption decreased and the desorption effect was more pronounced than the adsorption effect.[35] Qin *et al*. also presented a similar effect of temperature on adsorption efficiency.[36] The results verified that the process of adsorption was temperature dependent with an optimal temperature level of about 35 °C for the paper mill E_{OP} stream.

Agitation rate

The E_{OP} stream wastewater was treated with 10 g/100 mL dose of AC-CPW, AC-LC and AC-FC at different agitation rates in the range of 50 to 175 rpm, while the other variables were kept constant (temperature, contact time and pH as 25 °C, 3 h and 11.1), and the removal efficiency of colour and lignin was measured. With the increase in the agitation rate from 50 to 150 rpm, at 10 g/100 mL dose of AC-CPW, the colour and lignin removal efficiencies were improved from 88% to 91.7% and 78% to 79.7%, respectively. Beyond 150 rpm, the pollutants removal was reduced. In the case of commercial ACs, 67.1% to 68.4%, and 80.6% to 81.9% lignin removal was observed, and 63.0% to 74.9%, and 90.4% to 93.4% reduction in colour was determined, at 10 g/100 mL adsorbent dose of AC-LC and AC-FC, respectively, under the same adsorption conditions as above. The results are shown in Figure 3 (c), confirming that, once the equilibrium was achieved, further reduction was not observed in lignin and colour. Actually, at equilibrium, the adsorption rate is roughly comparable to the rate of desorption.[37]

Contact time

Contact time is considered one of the most important variables as it plays an essential role during adsorption.[32] The impact of varying contact times in the range of 1.0 to 10 h for 10 g/100 mL of different ACs in E_{OP} wastewater was investigated, while the other variables were kept constant (temp.: 25 °C, pH: 11.1 and agitation rate: 125 rpm). The effects of varying contact time on lignin and colour removal efficiencies are shown in Figure 3 (d). With increasing contact time, the lignin and colour removal efficiencies improved in the order: AC-FC- > AC-CPW > AC -LC. An increasing trend of % reduction was found up to 5 h, when AC-CPW and AC-FC achieved equilibrium, while for AC-LC it was found to be 7 h. After reaching equilibrium, the adsorption was observed to decrease up to 10 h and further enhancement was not noticed. It is believed that the primary step directs adsorption of pollutants on the surface of the adsorbent, and the consequent step directs gentle movement of pollutants from the bulk fluid on the adsorbent's external surface to internal sites, and adsorption progressively declines when the adsorption sites are entirely occupied.[38] The same trend was also reported in previous research.[39]

pH

The pH is another important parameter for adsorbing pollutants from effluent wastewater. The effect of pH was studied by varying the pH of the E_{OP} effluent in the range from 5.0 to 12.0 for 10 g/100 mL dose of different ACs, while the other variables were kept constant (temperature, contact time and agitation rate as 25 °C, 3 h and 125 rpm, respectively) for each batch of 100 mL effluent, and the results are presented in Figure 3 (e). The highest removal was found at 9 pH for all different ACs, with the following trend: AC-FC > AC-CPW > AC-LC. The removal of lignin and colour with AC-FC was enhanced from 78.5 to 84.3% and 88.0 to 94.0%, respectively, at pH 5 to 9, while the removal efficiency declined when pH increased from 10 to 12 at the same dose of ACs. This might be due to higher solubility of colour-contributing compounds and lignin at higher pH, decreasing the removal of pollutants.[40] The same trend of the removal efficiency with varying pH was found for both commercial ACs. The present study established that the adsorption efficiency of ACs for pollutants removal was affected by the pH of the effluent,[41] and demonstrated that the stream of E_{OP} effluent could be effectively treated at about 8-9 pH.

The data on removal efficiency of lignin and colour under optimized conditions are presented in Table 3.

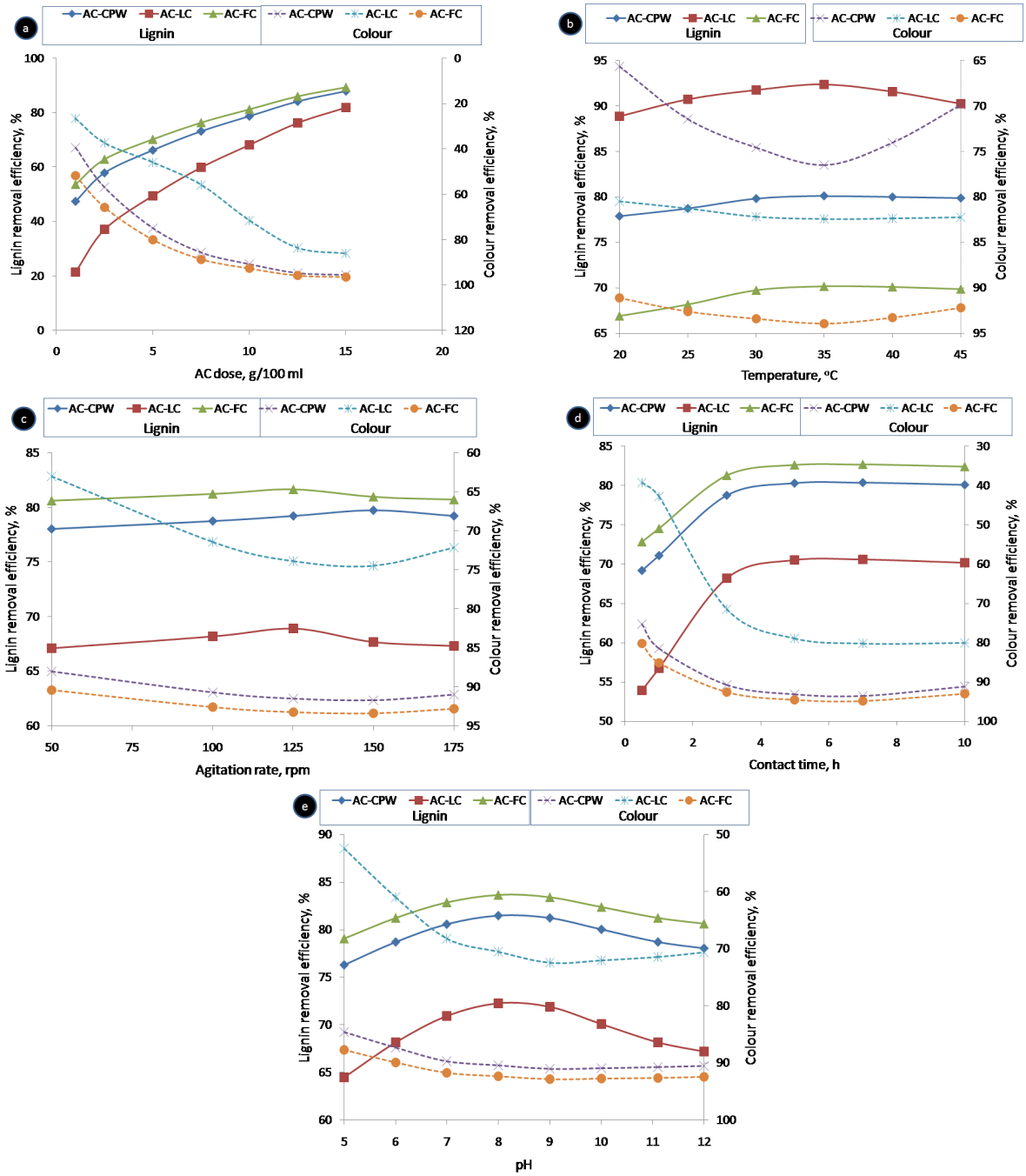

Figure 3: Adsorption efficiency of lignin and colour as a function of (a) adsorbent dose, (b) temperature, (c) agitation rate, (d) contact time and (e) pH

Table 3
Removal efficiency of lignin and colour under optimized conditions

AC type	Lignin removal, %	Colour removal, %
AC-CPW	82.7 ± 1.32	94.5 ± 2.71
AC-LC	74.8 ± 1.41	76.2 ± 2.65
AC-FC	83.2 ± 1.87	95.1 ± 2.20

Adsorption isotherm

The process of adsorption of pollutants (lignin and colour) on different ACs complies with the Langmuir as well as Freundlich isotherms as the plot of specific adsorption (Ce/qe) versus equilibrium concentration (Ce) and log x/m

versus log Ce were found linear (Fig. 4). Table 4 presents the values of subsequent isotherm parameters, such as their correlation coefficients (R^2) and q_{max} (mg/g), b (L/mg), n and K calculated through the slope and intercept of linear plots.

When examining the data using the Langmuir and Freundlich isotherms, it was found that, in terms of R^2, the Freundlich model was found to describe better the adsorption process than the Langmuir model, for AC-CPW, AC-LC and AC-FC. The above observation established that the Freundlich model fitted the data obtained in the experiments somewhat better than the Langmuir model. The results are in line with those presented by other researchers.[42] The Freundlich model is probably more suitable for studying the adsorption of pollutants from wastewater onto activated carbon, as it captures heterogeneous adsorption, it accounts for multilayer adsorption, allowing for non-ideal adsorption. Activated carbon has a highly porous and irregular structure, with a wide distribution of pore sizes and surface functional groups. This leads to varying adsorption affinities across the surface. Also, the E_{OP} stage wastewater is complex, containing high molecular weight organic compounds that can form multiple layers on the surface of the activated carbon. Lignin or other large organic molecules might adsorb in layers or in clusters on the surface, which the Freundlich model is better equipped to describe.

The equilibrium parameter (R_L) of the Langmuir adsorption isotherm was analyzed to predict the adsorbate and adsorbent affinity. The value of R_L in the present study was found to be 0.109-0.152 for lignin, and 0.015–0.046 for colour, which indicated that the pollutants adsorption on ACs was a favorable process. According to the Freundlich equation, the n value was 1.39–1.48 for lignin and 1.92-2.21 for colour, which was in agreement with the condition $n > 1$ that is the most general situation.[32] The n value between 1 to 10 is considered to be good adsorption,[43] and in the present study, the n value indicated that the adsorption of colour and lignin pollutants onto different ACs is a physical process.

Recently, another study also found that activated carbon from plastic PET (polyethylene teraphthalate) waste can be used as adsorbent for BPA (Bisphenol A) in aqueous solution.

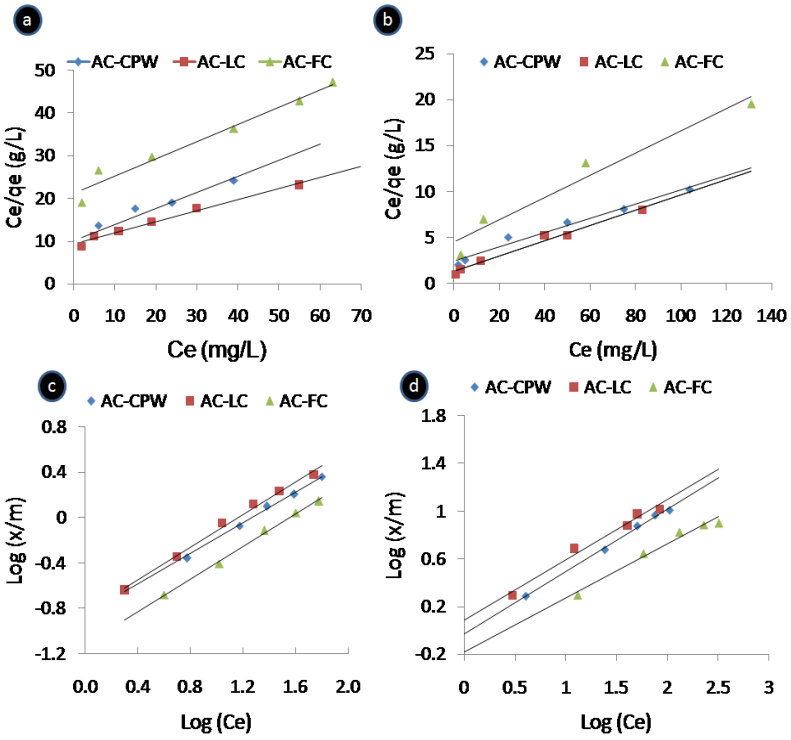

Figure 4: Linearised plots of Langmuir isotherm model for (a) lignin and (b) colour; Freundlich isotherm model for (c) lignin and (d) colour, with AC-CPW, AC-LC and AC-FC

Table 4
Isotherm parameters for colour and lignin adsorption onto AC-CPW, AC-LC and AC-FC

Isotherm model	Parameter	AC type	Predicted isotherm parameters			
			q_{max} (mg/g)	K (L/mg)	R^2	R_L
Langmuir	Lignin	AC-CPW	3.597	0.027	0.925	0.111
		AC-LC	2.475	0.019	0.964	0.152
		AC-FC	3.861	0.028	0.983	0.109
	Colour	AC-CPW	12.048	0.019	0.954	0.046
		AC-LC	8.264	0.056	0.977	0.016
		AC-FC	12.987	0.059	0.982	0.015
			n	K	R^2	
Freundlich	Lignin	AC-CPW	1.48	0.139	0.997	
		AC-LC	1.40	0.077	0.997	
		AC-FC	1.39	0.146	0.993	
	Colour	AC-CPW	1.92	0.944	0.997	
		AC-LC	2.21	0.660	0.975	
		AC-FC	1.98	1.224	0.979	

The data presented on the adsorption of BPA was found to fit better to the Langmuir equation rather than the Freundlich equation.[44] Other adsorbates, namely p-nitrophenol and Fe(III), have also been studied for adsorption onto activated carbon from PET.[45] Industrial wastewater has also been treated by using activated carbon produced from apple seed husks, oil seed and whole seed to eliminate dissolved and suspended particles.[46] Results showed that activated carbon from seed husks and oil seed was able to remove total suspended solids, total dissolved solids and biological oxygen demand of the wastewater significantly.[46]

To understand the potential differences in removal efficiency of lignin and color when treating E_{OP} stage wastewater from pulp and paper industry using the three types of activated carbon (AC-CPW, AC-LC, AC-FC), we need to consider the following key factors from the data: surface area, methylene blue (MB) number, and iodine number (IN). A higher surface area generally indicates a greater capacity for adsorption of organic pollutants like lignin and color compounds. AC-FC, with the largest surface area (905 m^2/g), is expected to have the best adsorption performance for both lignin and color due to more available active sites. AC-CPW had the second largest surface area. The MB number is indicative of the carbon's ability to adsorb large molecules. Lignin is a relatively large and complex molecule, so a higher MB value suggests better removal of lignin. Again, AC-FC, with the highest MB value, is likely to be the most efficient in removing lignin. AC-CPW had the second largest MB number. The iodine number measures the ability to adsorb smaller molecules and could correlate with the removal of color, which is often due to smaller organic molecules in the wastewater. AC-FC having the highest iodine number is expected to be most effective in color removal as well. AC-CPW had the second largest iodine number. The lignin and colour removal efficiency was valuable for E_{OP} wastewater and the adsorption trend was found as AC-FC > AC-CPW > AC-LC.

CONCLUSION

The present study on exploitation of AC made from CPW for pollutants removal from the E_{OP} stream of a paper and pulp mill revealed that AC-CPW had fine adsorbent characteristics in comparison with commercial ACs, *e.g.* AC-LC and AC-FC. The carbon activated by using $ZnCl_2$ enhanced the effectiveness of AC-CPW as adsorbent. The lignin and colour removal efficiency was valuable for E_{OP} wastewater and the adsorption trend was found as AC-FC > AC-CPW > AC-LC. Individual impacts of different variables, such as AC dose, effluent temperature, agitation rate, contact time and effluent pH, were considered to find the best conditions for the efficient removal of lignin and colour from the E_{OP} effluent. The use of AC resulted in a decrease of 82.7 ± 1.32% in lignin and 94.5 ± 2.71% in colour with AC-CPW under optimized conditions in comparison with AC-LC (reduction of 74.8 ± 1.41% in lignin and 76.2 ± 2.65% in colour) and AC-FC (reduction of 83.2 ± 1.87% in lignin and 95.1 ± 2.20% in colour), respectively.

The adsorption isotherms study in the present work concluded that the Freundlich model

presented a better fit for the data in comparison with the Langmuir model. The R_L value (less than one) from the Langmuir model confirmed the favorability of the adsorption of pollutants onto AC, and the n value from the Freundlich model indicated the physical nature of the process. In the future, economical manufacture of AC and its use for removal of wastewater pollutants could open a venue for efficient plastic waste management and subsequent treatment of wastewater.

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