Wastewater treatment using low cost activated carbons derived from agricultural byproducts—A case study

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Abstract

A variety of low cost activated carbons were developed from agricultural waste materials viz., coconut shell, coconut shell fibers and rice husk. The low cost activated carbons were fully characterized and utilized for the remediation of various pollutants viz., chemical oxygen demand (COD), heavy metals, anions, etc., from industrial wastewater. Sorption studies were carried out at different temperatures and particle sizes to study the effect of temperatures and surface areas. The removal of chloride and fluoride increased with rise in temperature while COD and metal ions removal decreased with increase in temperature, thereby, indicating the processes to be endothermic and exothermic, respectively. The kinetics of COD adsorption was also carried out at different temperatures to establish the sorption mechanism and to determine various kinetic parameters. The COD removal was 47–72% by coconut shell fiber carbon (ATFAC), 50–74% by coconut shell carbon (ATSAC) and 45–73% by rice husk carbon (ATRHC). Furthermore, COD removal kinetics by rice husk carbon, coconut shell carbon and coconut fiber carbon at different temperatures was approximately represented by a first order rate law.

Results of this fundamental study demonstrate the effectiveness and feasibility of low cost activated carbons. The parameters obtained in this study can be fully utilized to establish fixed bed reactors on large scale to treat the contaminated water.
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Keywords: Adsorption; Activated carbons; COD removal; Water/wastewater treatment; Rice husk; Coconut shells; Coconut shell fibers

1. Introduction

Industries have a large potential to cause lake, streams and river pollution. It is very difficult to generalize the industrial wastes unlike the domestic sewage. The nature of pollution varies from industry to industry and also from plant to plant. The organic content of wastewater is traditionally measured using lumped parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) [1–5]. These parameters, as such, do not indicate the specific chemical identities of the organic contaminants. Suspended substances, nutrients and organic contaminants as COD are major contributing pollutants. Various treatment technologies were utilized for organics removal from wastewater. The physicochemical techniques are widely used to treat wastewater in

various industries. These techniques include adsorption, chemical reaction, filtration, ion-exchange, coagulation/flocculation reverse osmosis, electrodialysis and so on [6–9]. Based on the level of treatment provided, wastewater treatment processes are frequently classified as preliminary, secondary or tertiary treatments. Voluminous literature is available on the applications of physicochemical techniques. Physicochemical processes have a number of advantages versus the biological and other treatment processes. Physicochemical treatment processes remain unaffected by the presence of toxic substances such as metals whereas biological systems fail to operate in case of wastes predominantly inorganic or non-biodegradable in nature.

In India, there are ~7500 industries of considerable pollutional significance and ~4500 of them have put up effluent treatment plants [10]. There are several tens of thousands of other small industries, which contribute significantly to pollution load but escape attention. Considerable amounts of wastewater is also generated as human waste or sewage. Removal

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of these contaminants from wastewater to adequate levels is one of the fundamental goals in waste treatment using various available technologies. However, conventional treatment technologies implemented in the industrialized nations are expensive to build, operate and maintain in developing countries. Therefore, efforts are still going on to develop affordable treatment technologies for developing and underdeveloped countries.

Various technologies to treat water/wastewater are very well documented [1–3,11–25] but few studies are reported which use of low cost adsorbents to clean organic loads together with some toxic inorganic metal cations and anions from industrial wastewater/effluents. Crittenden et al. [3] utilized granular activated carbon to remove dissolved organic carbon to reduce disinfection by-products. Biological treatments on COD remediation were reported by Kim et al. [13]. They evaluated the synergistic relationships using series of adsorption isotherms in terms of chemical oxygen demand. Simultaneous reduction in chromium and COD of tannery effluents by actinomycetes was studied by More et al. [26]. Bansode et al. [5] investigated adsorption efficiency of pecan shell-based granular activated carbon for the uptake of organic components responsible for the chemical oxygen demand (COD) of municipal wastewater. Fly ash, brick kiln ash and commercial activated carbon were utilized for COD remediation from domestic wastewater [27] with removal efficiencies of 88, 83 and 99%, respectively. Coconut coir, saw dust, and avocado peel carbons were also investigated for COD remediation [28,29]. Mixed adsorbent carbon (MAC) and a commercially available carbon (CAC) were utilized and removal efficiencies of 96 and 99% respectively, were achieved [30]. Bone char [31], activated carbons [32,33], were also investigated for COD remediation.

To comply with current stringent regulations and to restore a safe environment, it has become imperative to find some less costly, easily adaptable treatment technologies. For quite some time we (Industrial Toxicology Research center, Lucknow, India) have been involved in developing suitable low cost, efficient indigenous adsorbents/carbons capable of removing various pollutants from industrial effluents [34–39]. Low cost adsorbents for water/wastewater treatment have also been reviewed [40–42]. Continuing our activities, we have utilized some low cost activated carbons developed earlier [34–39] from coconut shells, coconut shell fibers, and rice husks for wastewater remediation. COD was chosen since the adsorption of COD was frequently studied to evaluate the overall adsorption behavior of the organics in wastewaters [13,43]. This study is likely to achieve the twin objectives of controlling environmental pollution by: (i) removal of pollutants from wastewater/effluents and (ii) utilization of three agricultural byproducts.

2. Materials and methods

All AR grade chemicals were used. Stock solutions of the test reagents were prepared to the desired concentration periodically, as and when required using double distilled water. The pH of the test solutions was adjusted using reagent grade dilute sulfuric acid and sodium hydroxide.

2.1. Equipments

The pH measurements were made with a pH meter (model 744, Metrohm). Electrical conductivity of the distilled water was measured with a conductivity meter (model 162A, Thermo-Orion, USA) as and when required. The metal concentrations in the samples were determined using an Inductively Coupled Plasma Spectrophotometer (model ICPAES-Labtam). Anions concentrations were estimated using Ion-Liquid Chromatograph (Model Metrohm micro devices). The N_2 isotherms were determined with a Quantachrome surface area analyzer (Model Autosorb-1). Agitation of the system under investigation was carried out on a thermostat-cum-shaking assembly (model MSW 275).

2.2. Chemical oxygen demand (COD) estimation

The chemical oxygen demand (COD) is commonly used to indirectly measure the amount of organic compounds in water/wastewater. In other words, COD is being used as a very useful parameter to measure the water quality of surface water (e.g. lakes and rivers). It is defined as a measure of the oxygen equivalent of the organic content of the sample that is susceptible to oxidation by a strong chemical oxidant and it is estimated according to APHA [44]. As COD measures the oxygen demand of organic compounds in the water samples, it is necessary that no organic material be accidentally added externally to the sample to be measured. Thus, a blank sample is always required in determining the COD. Blank sample was created by adding acid and oxidizing agent to a volume of distilled/deionized water. Thus, COD was measured for both the wastewater and blank samples, and the two were compared. The oxygen demand in the blank sample was subtracted from the COD for the original sample to ensure a true measurement of organic matter. In the present investigations, COD (mg/L) was determined using the Eq. (1)

$$COD = \frac{(b-a) \times (N) \text{ of ferrous ammonium sulfate } (100) \times (8)}{\text{Volume (ml) of sample}}$$

(1)

where b is the volume of ferrous ammonium sulfate (FAS) used in the blank sample, a is the volume of FAS in the original sample.

2.3. Adsorbents development and characterization

Coconut shells, coconut shell fibers and rice husks (agricultural by products) often present serious disposal problem for local environment. These raw materials were collected from Lucknow, India. One part of waste product (each separately) was treated with two parts (by weight) of concentrated sulfuric acid and kept in an oven at 150–165 °C for a period of 24 h. In this way, three types of activated carbons were derived. The carbonized materials were washed with doubly distilled water

to remove the free acid and dried at 105–110 °C for 24 h. The dried materials were subjected to thermal activation at 200, 400, 600 and 800 °C for 1 h. The products obtained at a temperature higher or lower than 600 °C exhibited less adsorption capacities probably (at higher temperature) due to collapse of surface functional groups. The activation was carried out under closely controlled conditions to obtain optimum properties. The temperature and time were optimized by characterizing the surface properties (e.g. surface area) of the activated products obtained by treating the raw materials for different time intervals at the temperatures mentioned above. More details about these carbons are reported elsewhere [34–37]. The carbons were cooled and sieved to desired particle sizes (30–200, 200–250 and 250–300 mesh). Finally, the products were stored in a vacuum desiccator until required. The analysis, characterization, and batch-to-batch reproducibility of the acid treated coconut shell carbon (ATSAC), acid treated coconut shell fibers carbon (ATFAC) and acid treated rice husk carbon (ATRHC) were strictly controlled. Carbons having 30–200 B.S.S. mesh size were used in sorption and kinetic studies unless otherwise stated.

Carbons were characterized by gas adsorption (N_2, -160 °C) and density measurements. The N_2 isotherms were determined in a Quantachrome surface area analyzer (Model Autosorb-1). About 0.10 g of sample was out-gassed at 250 °C for 12 h, prior to effecting adsorption measurements. The mercury density (ρ_{Hg}) (Eq. (2)) was measured by obtaining the sample volume by exclusion of the mercury volume from the volume of a previously calibrated glass cell. The helium density (ρ_{He}) was measured in a Quantachrome Stereopycnometer (Eq. (3)).

$$\rho_{Hg} = \frac{M}{V_s} \tag{2}$$

$$\rho_{He} = \frac{M}{V_s'} \tag{3}$$

where M is the mass of the sample, V_s the sample volume and V_s' is the sample volume inaccessible to helium.

Pores and internal surface are requisites for an efficient adsorbent. The specific surface area (S_{BET}) was evaluated from the N_2 adsorption isotherms by applying the Brunauer et al. equation [45] in the relative pressure (p/p^0) range and taking a_m (i.e., the average area occupied by a molecule of N_2 in the completed monolayer) to be equal to 16.2 Å^2. In addition, the micro- and mesopore volumes (V_{mi}, V_{me}) were obtained from the adsorption isotherms. V_{mi} was taken as the volume of N_2 adsorbed (V_{ad}) at $p/p^0 = 0.10$ and V_{me} as the volume of N_2 adsorbed (V_{ad}) at $p/p^0 = 0.95$ minus the V_{ad} at $p/p^0 = 0.10$. The micropore volume (W_0) was further estimated by applying the Dubinin–Radushkevich equation [46] and [47], as given by the equation:

$$\log W = \log W_0 - D \log^2 \left(\frac{p^0}{p} \right) \tag{4}$$

where W is the micropore volume that has been filled with liquid N_2 when the relative pressure is p/p^0 and W_0 is the total micropore volume. D is a characteristic constant of the micropore structure of the adsorbent. V_{mi}, V_{me} and W_0 were expressed

as liquid volumes. The total pore volume (V_T) was calculated by making use of the expression (5) and also (V_T') by summing up V_{mi}, V_{me} and V_{ma}.

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \tag{5}$$

IR spectra of the carbons were recorded using an IR spectrophotometer (Perkin-Elmer) in 500–4000 cm^{-1}. X-ray measurements were made using a Phillips X-ray diffractometer employing nickel-filtered Cu Kα radiation.

2.4. Wastewater collection

Wastewater samples were collected from the outlet of an industry located at Jagdishpur, Uttar Pradesh, India. Samples were collected as per standard methods [44], and transported immediately to the laboratory (Industrial Toxicology Research Centre, Lucknow, India) under standard conditions. Samples were processed and analyzed by standard methods.
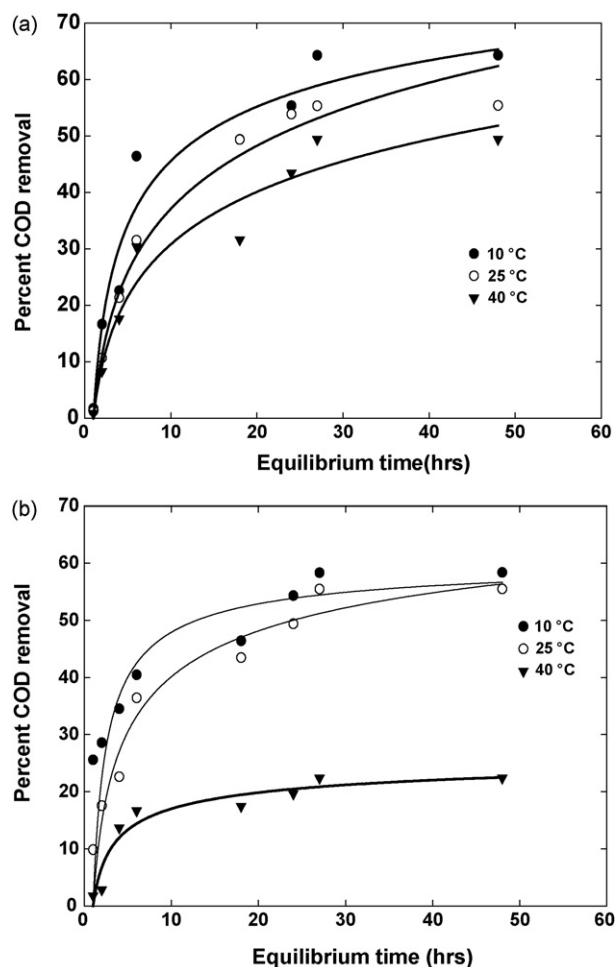

Fig. 1. Variation of COD removal rates on activated carbons derived from (a) coconut shells and (b) rice husks.

Table 1
Characteristics (S_{BET}, microporosities (N_2 at 77 K), pore volumes and densities) of activated carbons derived from agricultural waste materials

Sample	S_{BET} (m² g⁻¹)	V_{mi} (cm³ g⁻¹)	W_0 (cm³ g⁻¹)	V_{me} (cm³ g⁻¹)	V_{ma} (cm³ g⁻¹)	ρ_{Hg} (g cm⁻³)	ρ_{He} (g cm⁻³)	V_T (cm³ g⁻¹)	V_T' (cm³ g⁻¹)
ATFAC	512	0.17	0.18	0.07	0.29	1.65	0.84	0.58	0.53
ATSAC	380	0.12	0.13	0.05	0.19	1.60	0.91	0.47	0.36
ATRHC	17.2	0.006	0.005	0.017	0.30	0.91	1.61	0.48	0.32

$V_{me} = V_{cu}$ (at $r = 10$ Å) $- V_{ma}$, $V_{ma} = V_{cu}$ (at $r = 250$ Å), V_{cu} = cumulative pore volume (mercury porosimetry), $V_T = 1/\rho_{Hg} - 1/\rho_{He}$, ρ_{Hg}, $V_T' = V_{mi} + V_{me} + V_{ma}$.

2.5. Sorption procedure

2.5.1. Kinetic studies

Batch kinetic tests were performed to determine the COD adsorption kinetics. For this purpose, a series of 1 L conical flasks were employed. Each flask was filled with 500 mL of effluent and was placed in a thermostat controlled shaking assembly. When the desired temperature was reached, a known amount of carbon (20 g) was added into each tube and the solutions were agitated by shaking. At pre-decided time intervals, the solutions of the specified tubes were separated from the adsorbent and analyzed to determine COD uptake.

2.5.2. Equilibrium studies

Batch sorption studies were performed at different temperatures (10, 25 and 40 °C) to obtain the equilibrium data required for the design and operation of column reactors for treatment of wastewater/effluent. For equilibrium studies, a series of 1 L conical flasks were employed. Each flask was filled with 500 mL of effluent. A known amount of activated carbon (20 g) was added into each flask and agitated intermittently for the desired time periods, up to a maximum of about 48 h. The contact time and other conditions (e.g. adsorbent dose) were selected on the basis of preliminary experiments that demonstrated that the equilibrium was established in 48 h (Fig. 1). After this period the solution was filtered using Whatman No. 1 filter paper and analyzed for COD, anions and metal ions.

3. Results and discussion

3.1. Characterization

X-ray spectra (not provided in the manuscript) of developed carbons (ATSAC, ATFAC, ATRAC) did not show any peak thereby indicating the amorphous nature [34–37]. One-gram of each carbon sample was stirred with 100 mL of deionized water separately at a pH of 6.8 for 2 h and left for 24 h in an airtight stoppered conical flask. A slight increase in pH was observed. SEM micrographs (reported earlier) revealed the surface texture and different porosity levels in the materials under study [34–37]. The values of surface area (S_{BET}), V_{mi}, V_{me}, V_{ma}, W_0, V_T, ρ_{He}, ρ_{Hg} are listed in Table 1. The different chemical constituents of developed carbons are provided in Table 2 along with some other characteristics.

The IR spectra of activated carbons indicated weak and broad peaks in the region of 3853–453 cm⁻¹. Approximate FT-IR band assignments indicated the presence of carbonyl, lactones, and phenols. The 1800–1540 cm⁻¹ band is associated to C=O

Table 2
Compositions and pH's of activated carbons derived from agricultural waste materials

Characteristics	ATSAC	ATFAC	ATRHC
Ash (%)	6.26	7.22	7.80
pH	5.72	5.80	5.90
C	76.64	76.38	75.23%
N	0.28%	0.38%	0.28%
H	2.20%	1.95%	1.78%

stretching mode in carbonyls, carboxylic acids, and lactones, while 1440–1000 cm⁻¹ band was assigned to the C–O stretching and O–H bending modes such as phenols and carboxylic acids [34–37].

The wastewater characteristics, collected from the outlet of a chemical industry located at Jagdishpur, U.P., India are given in Table 3.

3.2. Kinetic studies

The COD uptake was increased with increase in adsorbent dosages (data omitted for brevity). There is a substantial increase in COD removal when the carbon dosage increased from 10 to 20 g/L, while the increase on introducing additional 10 g/L of carbon was not significant. Thus, the amount of carbon has been kept 20 g/L in all the subsequent sorption and kinetic studies. The contact time and other conditions were selected on the basis of preliminary experiments that demonstrated that the equilibrium was established in 48 h. Equilibrium for times between 48 and 72 h gave practically same uptake. Therefore, the contact

Table 3
Physicochemical characteristics of industrial wastewater

Parameters	Values (g/L) except pH
pH	7.35
Total solid	1360
Dissolved solid	1100
Suspended solid	260
COD	553
BOD	260
Fluoride	0.507
Chloride	164
Iron	0.244
Manganese	8.12
Lead	16.08
Zinc	17.05
Chromium	0.31
Zinc	0.33

time was kept 48 h in all the equilibrium and kinetic studies. The removal of COD at different temperatures is presented in Fig. 1. COD removal takes place in two phases. First phase of COD uptake "the immediate COD removal", obtained within a few hours, is followed by "subsequent removal" of COD and this continues for a longer period. This can be mathematically represented as follows (Eq. (6))

$$\Delta S = \Delta S_i + \Delta S_t \tag{6}$$

where ΔS is the total COD removal in time "t" at a given concentration of C_0 and C_f while ΔS_i is the COD removed in the first phase when the process is quite fast and ΔS_t is the amount of COD uptake in the second phase. It is clear from Fig. 1 that more than 50% adsorption occurs within 8–10 h of the contact time while remaining adsorption occurs in 38–40 h.

COD removal kinetics can be evaluated using Eq. (7) [48,49].

$$\Delta S = k_t \times t^m \tag{7}$$

where ΔS is the percent COD removal, k_t and m are the constants. A fairly linear relationship between the log of the percent COD removal versus the log of time is obtained (Fig. 2). The numerical values of m and k_t, obtained using Eq. (7) are given in Table 4. Similar results were reported earlier [4,48,50].

According to Weber and Morris [51], a value of $m = 0.5$ reflects "intraparticle diffusion" as the rate determining step. Generally, solute uptake on adsorbents like activated carbon involves two processes. One is the transport of adsorbate from solution to particle solution interface and second is the adsorption on the accessible surface of adsorbent particle. If intraparticle diffusion is the rate-determining step, the value of "m" in the kinetic plots should be 0.5, while smaller values indicate the involvement of both the processes to almost an equal extent. In the present study, the value of "m" is either more then 0.5 or less then 0.5, indicating that sorption rate dependents on both and neither of these appear to be sufficiently slow as to be rate determining step. This is in conformity with the findings of Srivastava et al. [50].
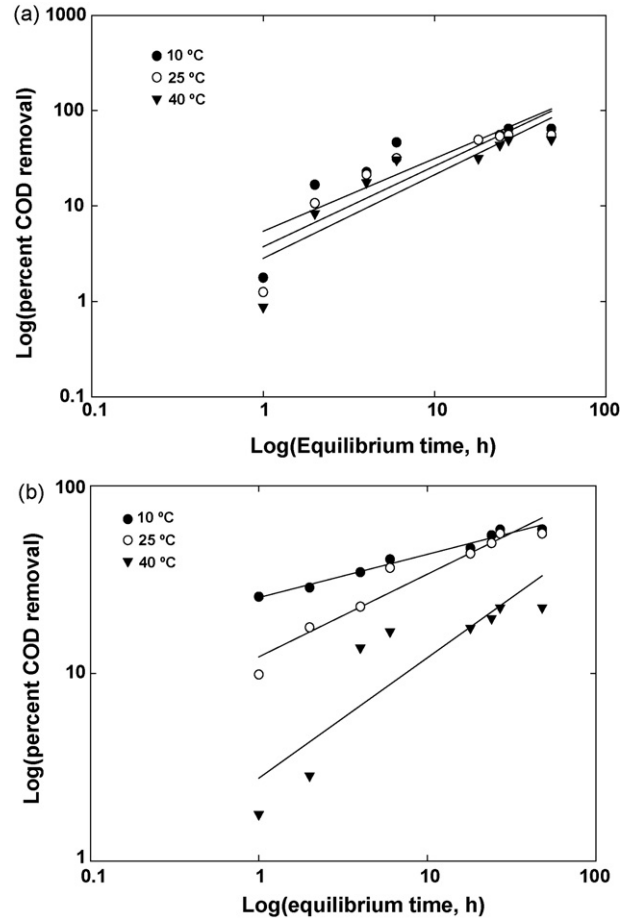
Fig. 2. Logarithmic rates of COD uptake on activated carbons derived from (a) coconut shells and (b) rice husks.

The kinetic equation can be obtained using Eq. (7) in the following manner [48]:

$$\frac{dC}{dt} = \frac{-kC_0}{[1 - (C/C_0)]^n} \tag{8}$$

where C_0 and C are initial and transient COD concentrations. The rate constant k_t and the order of reaction, n, can be calculated

Table 4
COD kinetics constants (m and k_t)

Adsorbents	10 °C			25 °C			40 °C		
	m	k_t	R^2	m	k_t	R^2	m	k_t	R^2
Rice husk carbon	0.6417	0.4405	0.7907	0.4408	1.087	0.9342	0.2303	1.4039	0.9749
Coconut shell carbon	0.5211	0.9005	0.8680	0.5155	0.9911	0.9045	0.4257	1.161	0.8602

Table 5
Rate constants and order of reaction for COD removal

Adsorbents	10 °C		25 °C		40 °C	
	k (h^{-1})	n	k (h^{-1})	n	k (h^{-1})	n
Rice husk carbon	0.178	1.55	0.5328	1.26	1.00	3.34
Coconut shell carbon	0.4432	0.919	0.5067	0.9390	0.6046	1.34

using Eqs. (9) and (10)

$$k = m k_t^{1/m} \tag{9}$$

and

$$n = m^{-1} - 1 \tag{10}$$

The rate constants and reaction orders are given in Table 5. From the data reported in Table 5, the kinetics of COD removal by rice husk carbon, coconut shell carbon and coconut shell fiber carbon at different temperatures can approximately represented by a first order rate equation except for the rich husk at 40 °C where abnormally very high value is obtained.

3.3. Sorption studies

Odor is recognized as a quality factor affecting acceptability of drinking water/wastewater. Most organic and some inorganic chemicals contribute taste and odor. These chemicals may originate from municipal and industrial waste discharges, from natural sources such as decomposition of vegetable matter, or from associated microbial activity, and from disinfectants or their products. Therefore, removal of odor is very important. The developed activated carbons used in the present study were able to remove the odor completely.

Suspended substances play an important (and often under estimated) role in characterizing the treatability and hence the degree of contaminant removal from water/wastewater. Therefore, removal of suspended solids (SS) is required steps in wastewater treatment. Filtration of SS using developed adsorbents was conducted and treatment efficiencies were achieved in the range of 70–80%. Maximum suspended solid removal was achieved with rice husk carbon.

Chloride and fluoride ions, are the major anions affecting water and wastewater quality. The adsorption of these anions was successfully carried out on coconut shell activated carbon (ATSAC), coconut fiber activated carbon (ATFAC) and rice husk activated carbon (ATRHC) at temperatures of 10°, 25°, and 40 °C (Fig. 1a and b). Best removal was achieved by coconut shell fiber carbon (ATFAC) followed by coconut shell carbon (ATSAC) and rice husk carbon (ATRHC). Removal of chloride and fluoride ions increases with temperature, indicating the process to be endothermic. Highest removal of both the anions was achieved with coconut fiber carbon at 40 °C (Fig. 3a and b).

Removal of various metal ions was also carried out on these three activated carbons at temperatures of 10°, 25°, and 40 °C. The results are presented in Fig. 4(a–d). The adsorption of iron, manganese and lead increases with a rise in temperature, confirming the endothermic nature of this sorption process. In contrast, zinc adsorption is an exothermic process. In case of lead, rice husk activated carbon worked well both at 10° and 25 °C while carbon made from coconut shell worked only at 10 °C. The activated carbon developed from coconut shell fibers was not able to remove lead from wastewater effluents. The most significant removal of zinc (50%) was achieved by coconut shell carbon while maximum iron removal (61%) was obtained using the activated carbon developed from coconut shell fibers.
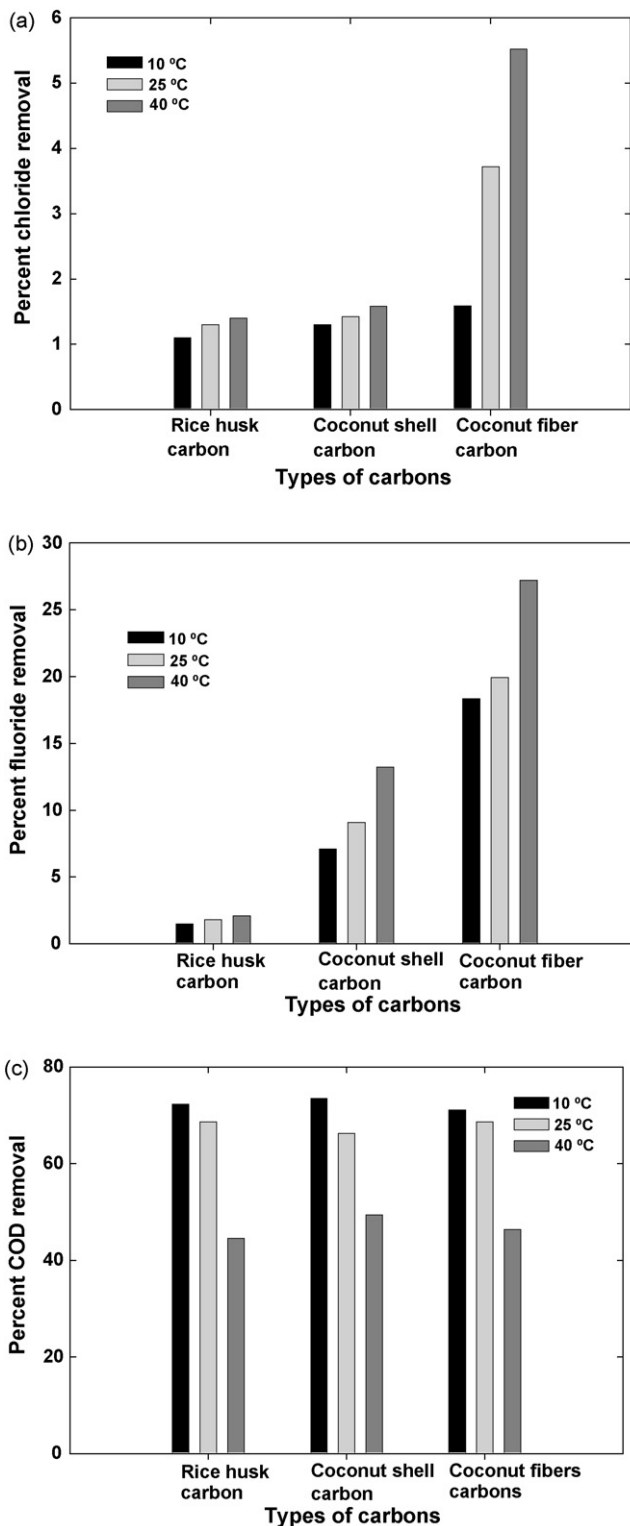

Fig. 3. Removal of (a) chloride, (b) fluoride and (c) COD on developed activated carbons.

The variation in COD adsorption with hydronium ion concentrations was also studied by obtaining the COD removal at pH values of 2.0, 4.0, 6.0, 8.0 and 10.0. In acidic range, increasing pH values do not influence the COD adsorption and the uptake almost remains constant in the pH range of 2.0–6.0. There
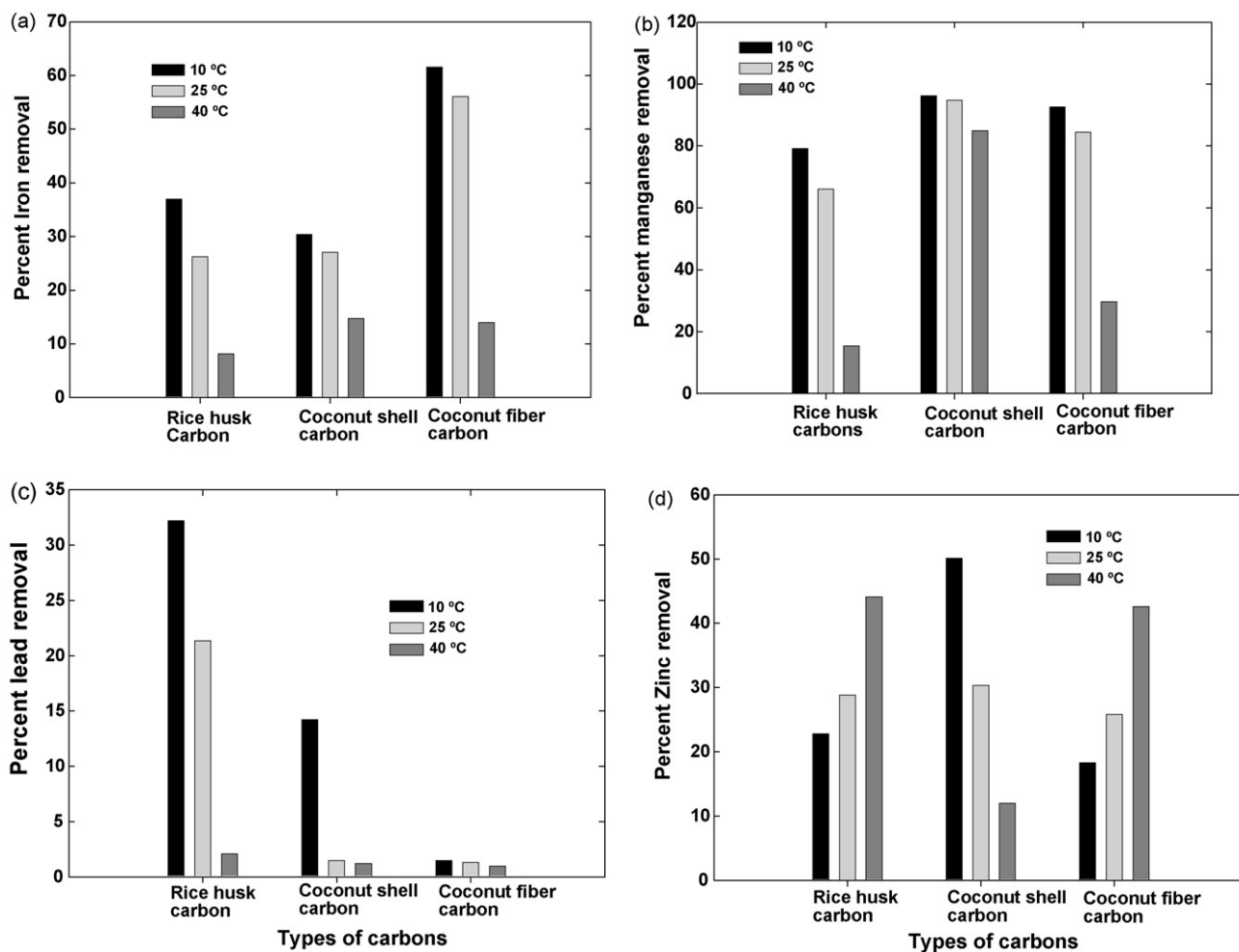
Fig. 4. Removal of (a) iron, (b) manganese, (c) lead and (d) zinc using developed carbons.

Table 6
Comparison of developed activated carbons vis-à-vis other adsorbents for COD remediation

Adsorbent Types	Type of wastewater	Initial COD concentration (mg/L)	pH	Adsorbent dose (g/L)	COD removal (%)	References
Coconut shell carbon (ATSAC)	Industrial (mixed)	553	6.0	40	46–71	Present study
Coconut fibers carbon (ATFAC)	Industrial (mixed)	553	6.0	40	50–74	
Rice husk carbon (ATRHC)	Industrial (mixed)	553	6.0	40	45–73	
Avacado peel carbon (APC)	Processing	22,000	7.0	40	98	[28]
Commercially available carbon (CAC)	Processing	22,000	7.0	40	99	
Fly ash	Domestic	1080	2.0	40	88	[27]
Brick kiln ash	Domestic	1080	5.0	60	83	
Commercial carbon	Domestic	1080	2.0	45	99	
Mixed adsorbent carbon (MAC)	Domestic	1080	7.0	35	96	[30]
Commercial carbon (CAC)	Domestic	1080	2.0	40	99	
Carbon developed from fertilizer waste	Industrial	8000	4.0	30	~50	[4]
Blast furnace slag	Industrial	8000	4.0	30	~70	
Filtrasorb 200 (F-200)	Municipal wastewater	40–67	7.55	15	~80	[33]
Pecan shell-based steam activated carbon (PSS)	Municipal wastewater	40–67	7.55	15	~85	
Pecan shell-based carbon dioxide-activated carbon (PSC)	Municipal wastewater	40–67	7.55	15	~70	
Pecan shell-based acid activated carbon (PSA)	Municipal wastewater	40–67	7.55	15	~90	
Acid activated coconut shell carbon	Beverage industrial wastewater	620–3470	7.22–7.24	30		[52]
Barium chloride-activated coconut shell carbon	Beverage industrial wastewater	620–3470	7.22–7.24	30		
Calgon carbon, F-300	Beverage industrial wastewater	620–3470	7.22–7.24	30	~70	

after a fall in COD removal was obtained (Figure omitted for brevity). A higher adsorption at low pH (or in acidic pH) results from the neutralization of negative charges at the surface of the adsorbents with increasing hydronium ion concentrations. This reduces the hindrance to diffusion and makes available more of the active surface to the various organic contaminants contributing to COD. At higher pH (pH > 6.0), COD adsorption decreased due to the abundance of OH^- ions, causing increased hindrance to diffusion of organics. In view of this, all the adsorption and kinetic studies were carried out at pH 6.0 to determine the removal efficiency of the developed activated carbons at or near the effluents pH. The removal of COD was 47–72% with coconut shell fiber carbon, 50–74% in case of coconut shell carbon and 45–73% for rice husk carbon as shown in Fig. 2. Sorption studies were also conducted at 10°, 25° and 40 °C. COD removal decreases significantly with increasing temperature, confirming that COD adsorption process is exothermic. Similar observations have been reported earlier [4,27,30].

4. Conclusions

The activated carbons were developed from agricultural waste materials. These were characterized and utilized for the removal of metals, chloride, fluoride and COD from industrial effluents. COD was chosen as the characteristic parameter and was examined in detail. The COD removal kinetics by rice husk and coconut shell carbons at different temperatures were approximately represented by a first order reaction. This fundamental study opened new dimensions on the utilization of low cost activated carbons developed from agricultural byproducts for water/wastewater remediation. Utilization of these agricultural waste materials will definitely reduce environmental burdens as well as the cost of treatment.

Furthermore, it is very difficult to directly compare the percent COD removal by the developed carbons versus the other adsorbents and commercially available carbons used for wastewater treatment due to a lack of consistency in literature data. COD removal was evaluated at different pHs, temperature, initial COD concentrations, particle size of the adsorbent and solid to liquid ratios. In other words rigorous direct comparisons of the tested adsorbents are difficult. Considering the above-mentioned facts, efforts are being made to compare the tested adsorbents indirectly by providing the optimum parameters (dose, initial COD concentrations, dose, pH) used for the COD removal. The percent COD removal capacities of various adsorbents and commercially available carbons are summarized in Table 6. The removal capacities of developed carbons viz., ATSAC, ATFAC and ATRHC are comparable/higher to the other tested adsorbents.

The results obtained in the laboratory scale study demonstrate the effectiveness and feasibility of these carbons which can be fruitfully applied for field applications. The overall quality of the treated water was ideal for the irrigation purposes and/or discharge into the lakes/streams. The recovery of the valuable metals and adsorbent regeneration, without dismantling the fixed bed adsorbers, are in progress to further bring down the process cost.

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