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Research paper

Utilization of cotton plant ash and char for removal of 2, 4-dichlorophenoxyacetic acid

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Abstract

Cotton is a common Indian crop grown on a considerable portion of farmland across the country. After separating the useful product (cotton fibers), the other parts of the plant (stalks, leaves, etc.) are discarded as wastes. In most cases, these plant materials are used as fuel in boilers or households. Cotton wastes when ignited in the presence and absence of air produce cotton plant ash (CPA) and cotton plant char (CPC), respectively. However, CPA and CPC produced pose environmental problems such as safe disposal. Thus, there is an urgent need to characterize the physical and chemical properties of these derivatives and to identify their potential uses. This study highlights the potential utilization of CPA and CPC as adsorbents of 2,4-D. The main components in CPA, namely, CaO and K_2O, provide micronutrients to the soil and are thus useful as a biofertilizers. Moreover, low manufacturing cost and higher availability favor the use of CPA as an efficient, low-cost adsorbent as well as a potential source of vital micronutrients. The adsorption capacity of CPA and CPC was tested using 2,4 dichlorophenoxyacetic acid (2,4-D) as the representative herbicide. Experimental data were analyzed by Freundlich and Langmuir adsorption isotherms, and these fitted well with the Langmuir model. The adsorption capacity q_0 was found to be 0.64 mg/g for CPA and 3.93 mg/g for CPC. Pseudo-first-order pseudo-second-order and intraparticle diffusion kinetic models were applied to experimental data, and the pseudo second order kinetics model showed best fit for the adsorption of 2,4-D on CPA and CPC. Both CPA and CPC were characterized using proximate analysis, SEM images, BET surface area, XRF, FTIR, and CHNS. The BET surface area was found to be 2 and 109 m^2/g, respectively, for CPA and CPC. Adsorption study results indicated that both CPA and CPC are very effective cheap adsorbent for 2,4-D removal.

Keywords: Cotton stem; 2,4-D; Adsorption; Isotherms; Kinetics; Characterization

1. Introduction

Cotton plant belongs to genus *Gossypium* (Family: *Malvaceae*). India is the second largest producer of cotton after China [1]. Annual production of cotton in India reported to be 68 million tons for 2013–2014 [2]. Cotton is a major crop cultivated all over India. Cotton (the soft white fibrous substance) is mainly used to make myriad of textile products. Cotton is also used in, the manufacture of explosives (nitrocellulose), cotton paper and in book binding. The stalk of cotton is used for production of papers [3].Cotton biomass is used to make briquettes [4], for adsorption of methylene blue [5]. Cotton seed another important by-product is used to produce cottonseed oil, which after refining is consumable like other vegetable oils [6]. Raw cotton contains non cellulosic components such as waxes, pectin, proteins, and hemicelluloses which can be extracted and used for various purposes [7]. After removal of economically profitable cotton flowers, whole cotton stem along with its leaves considered as a waste, and in most cases is burnt in the farmland or in open landfills. This cotton waste can be reduced by burning it in presence of oxygen or by pyrolysis which will produce cotton plant ash and cotton plant char (CPA and CPC), respectively. The ash thus produced can be added to soil to improve its micronutrient content, water-holding capacity, texture, bulk density, pH, and biological properties [8]. Similarly biochar which is prepared by biomass

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pyrolysis in the absence of oxygen is also used as soil additive. It is used globally as a method to improve soil fertility and to mitigate climate change [9,10].

2,4-D has been used as an herbicide in the agricultural sector. It acts as an anti-weed for plantation crops such as sugarcane, oil palm, cocoa, and rubber. It is a low-cost herbicide and is selective in activity. It is considered moderately toxic and its maximum allowable concentration in drinking water is 20 ppm [11]. However, 2,4-D is poorly biodegradable and has been frequently detected in water bodies in various regions around the world [12]. Several methods have been suggested for removal of 2,4-D, including adsorption [13,14], photo catalytic degradation, a combination of photo-Fenton and biological oxidation, advanced oxidation processes, aerobic degradation, nanofiltration membranes, ozonation, coagulation, fluid extraction, and solid-phase extraction [15]. Among these methods, adsorption is the best method to remove 2,4-D efficiently and economically.

In general the amount of biomass produced during cotton production is about four times as that of the fiber itself, however this biomass (stalk, leaves, etc.) is generally discarded as a waste or is only used for combustion. After combustion of stalk and leaves in boilers, ash is produced which is a potential waste. This generated waste possesses environmental challenges such as its safe disposal. It has been proven that biomass char has potential uses in various fields. One such use is that it can be a good and cheap adsorbent of various toxic compounds. Biomass ashes have been previously used as an adsorbent for the removal of pesticides from aqueous solution. Mustard plant ash has been reported as a rich source of micronutrients, and as an adsorbent of 2,4-D thus its addition serves dual purpose: improves crop yield, while simultaneously acting as an adsorbent to remove 2,4-D when spread on agricultural lands [14]. However, direct burning of biomass in an oxygen atmosphere has its own limitations. Because direct combustion results in oxidation of all carbons in the biomass, the biochar produced has limited adsorption capacity; by contrast, when the biomass is combusted in the absence of air, carbon-rich char is formed. According to some studies, materials with high carbon content show high adsorption capacity [16]. In addition, direct combustion of biomass causes inefficient use of energy. It has been proposed that instead of using direct combustion, pyrolysis of biomass would be more efficient. Pyrolysis of biomass releases significant amount of gases such as hydrogen, CO, and methane, which can act as more efficient fuels [17].

This study focuses on the characterization of CPA and CPC, and batch adsorption studies were performed to evaluate the adsorption capacity of CPA and CPC for 2,4-D. Besides, various operational parameters of adsorption were studied in depth. CPA and CPC were characterized by X-ray fluorescence (XRF), proximate analysis, CHNS analysis, Brunauer–Emmett–Teller (BET) surface area analysis, scanning electron microscopy (SEM), and Fourier transform-infrared (FTIR) methods. The study used locally available cotton waste as a source of micronutrient (CPA), carbon-rich material (CPC), and as an adsorbent for 2,4-D (CPA and CPC).

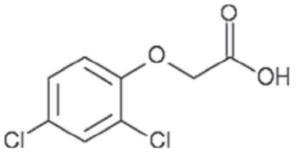
2. Materials and methods

2.1. 2,4-Dichlorophenoxyacetic acid

Technical-grade (98% pure) 2,4-D (Sigma–Aldrich, Malaysia) was used as obtained in this study. Milli-Q water (conductivity of Milli-Q water = 18.2 MΩ·cm at 25 °C) was used in the preparation of all the solutions. The molecular formula and properties of 2,4-D are as follows:

Properties of 2,4-D [14]

Molecular formula	$C_8H_6Cl_2O_3$
Molecular weight	221 g/mol
Solubility in water	0.90 g/L



2.2. Preparation of ash and char

Cotton plant remains i.e. stems were sun dried for a month and then burnt in open, the residue i.e. cotton plant ash thus produced was allowed to cool at 30 °C it was screened by BSS sieve no. 25 for removal of unburned particles. Further upon cooling this ash is packed in airtight polythene bags. This is called as CPA. CPA was rinsed almost 6 times with Milli-Q water until washed water came clear, then it was dried in oven at 110 °C for 24 hrs. All further studies were done by this sample.

Similarly for CPC, well dried stalks were ground and passed through BSS sieve no. 25. Powdered stalks were rinsed 6 times with double-distilled water, until the water used for washing becomes clear, and then dried in an oven at 110 °C for 24 hrs. The powdered shells were pyrolyzed in a vertical downdraft two-stage fixed-bed biomass reactor under steady nitrogen flow of 300 $cm^3\ min^{-1}$ at 650 °C with heating rate of 20 °C min^{-1}. Carbonization temperature was, maintained for 2 hrs. Formed char was collected in airtight plastic bags to avoid moisture contamination.

3. Batch adsorption study

Adsorption studies were carried out separately for CPA and CPC and effect of variation of following parameters were studied: adsorbent dose, initial concentration of 2,4-D, and contact time. Based on experimental data, kinetics and equilibrium models were studied and respective results were obtained. Batch adsorption studies were carried out using 25 ml 100 ppm of 2, 4-D solution with different amounts of CPA and CPC varying from 1gm to 8gm and 0.1gm to 1gm respectively. Dose optimized from this study was tested for different concentrations of 2, 4-D varying from 400 ppm to 50 ppm. Flasks were agitated in an isothermal water bath shaker at a constant speed (30 °C) for 20 hours. The initial and equilibrium concentrations of solution were measured by double-beam UV/VIS spectrophotometer (Shimadzu, Japan) at 283 nm [14]. Experiments were performed in triplicate sets and deviations were found to be within 1–3%. The amount of adsorption equilibrium was calculated using the following equation:

$$q_e = \frac{(\mathrm{Co} - \mathrm{Ce})\,\mathrm{v}}{\mathrm{W}} \qquad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of 2,4-D at initial and equilibrium, respectively; v(L) is the volume of the solution; and w(g) is the mass of dry adsorbent used. For the kinetic study, concentrations of 2,4-D at time t and equilibrium are denoted as q_t and q_e(mg/g), and are calculated as follows:

$$\mathrm{q_t} = \frac{(\mathrm{C0} - \mathrm{Ct})\,\mathrm{v}}{\mathrm{W}} \qquad (2)$$

The percentage of 2,4-D adsorbed is calculated using the following equation:

$$\%2,4 - \mathrm{D\ adsorbed} = \frac{100(\mathrm{Co} - \mathrm{Ce})}{Co} \qquad (3)$$

Experimental data were tested against linearized equations of the models such as Langmuir, Freundlich isotherms. In order to determine the isotherm parameters and the best fit of experimental data against the model predictions, the coefficient of determination (R^2) was calculated and error analysis was carried out by estimating the normalized deviation (ND) and normalized standard deviations (NSD) [18] as seen in Eqs. (4) and (5). $qe_{(exp)}$ and $qe_{\ (pred)}$ are the experimental and predicted urea sorption capacity (mg·g−1), respectively, and n is the number of observations made.

$$ND = \frac{100}{n}\sum\left|\frac{q_{e(\exp)} - q_{e(pred)}}{q_{e(\exp)}}\right| \qquad (4)$$

$$ND = 100\sqrt{\frac{\sum\left(\frac{q_{e(\exp)} - q_{e(pred)}}{q_{e(\exp)}}\right)^2}{n}} \qquad (5)$$

4. Characterization study

To describe properties of CPA and CPC, detailed characterization was carried out. Both samples were hand ground with a ceramic mortar and pestle to completely pass through a 200-mesh sieve and dried at least overnight at 105 °C prior to characterization and batch experiments. Proximate analysis was done by using gravimetric method. BET surface area was measured using Smart Instruments Co. Pvt. Ltd (India) by nitrogen adsorption desorption technique at 77K, CHNS analysis was performed on an Elemental Analyzer (vario MACRO Cube, Elementar, Munich, Germany), FTIR spectra were obtained using Spectrum One FTIR spectrometer (Perkin Elmer) and SEM images were obtained using JSM 6380A (JEOL, JAPAN). For XRF analysis, PAN analytical Model No. PW2403 was used. Solution pH was measured after shaking 0.5 gm of ash and char separately in 50 ml water for 24 hours. pH was measured using a pH meter (Model-pH 2700; Eutech, China).

5. Results and discussions

5.1. Characterization results

Proximate analysis of CPA and CPC was carried out using the Indian standard method for proximate analysis [19] and the results are tabulated in Table 1.

The results obtained showed that the proportion of fixed carbon in CPC is far greater than that in CPA. High percentage of carbon is attributed to pyrolysis in the absence of oxygen, which increases the adsorption capacity of char. Moreover, the solution pH of CPA and CPC, which were shaken with water for 24 hours separately, is highly alkaline, that is, the pH after 24 hours is 10.6 and 9.5, which indicates the basic nature of CPA and CPC surface. CHNS values indicated high amounts of organic carbon in CPC (61%) and high amount of ash in CPA (77%).

The BET surface area of CPA and CPC was found to be 2 and 109 m^2/g, respectively. The surface area of CPC is 54 times more than that of CPA, as it was pyrolyzed in the absence of oxygen. It has been reported that when biomass is exposed to high temperatures (e.g., 650 °C) for longer periods, all volatile matters are released from the biomass; moreover, this heat treatment generates tars, which is responsible for the increased surface area and high porosity [20]. By contrast, in the case of open combustion of biomass, such high temperatures are never attained and all carbon contents are completely burned, so chars produced by open combustion have smaller surface area.

We also analyzed the FTIR spectra of 2,4-D, CPA, and CPC to evaluate their surface characteristics. Fig. 1 shows the FTIR spectra of 2,4-D (A), CPA before adsorption (B), CPA after adsorption (C), CPC before adsorption (D), and CPC after adsorption (E).

The FTIR spectra of 2,4-D (Fig. 1, spectrum A) shows a peak at 1732 cm^{-1}, which indicates the presence of C═O of the carboxyl group [14]. The antisymmetric and symmetric vibrations of C—O—C are represented by the bands at 1311 and 1089 cm^{-1}, respectively, whereas the band due to O—H deformation coupled with C—O stretching vibration is observed at 1234 cm^{-1} [21]. The peaks at 1475 and 1435 cm^{-1} correspond to the C═C vibrations of the aromatic ring and CH_2 vibrations of alkanes, respectively [22]. The peak at 693 cm^{-1} is an indication of C—Cl stretching [23].

Spectra of CPA before adsorption (Fig. 1, spectrum B) show peaks between 1400 and 1450 cm^{-1}. Bands characteristic of calcium carbonate occur at 770–870 cm^{-1} and 1400–1450 cm^{-1}.

Table 1
Properties of CPC.

Parameter	CPA	CPC	Error (%)
(BET) Surface area, m^2/g	2	109	±3
Moisture content, %	1.22	2.79	±1
Volatile matter,%	21.12	6.71	±2
Ash,%	77.12	6.98	±1.5
Fixed carbon, %	0.54	83.52	±4
C, %	7.22	61	±2
H, %	0.7	1.32	±2
N, %	0.03	0.86	±2
S, %	0.1	0.22	±2

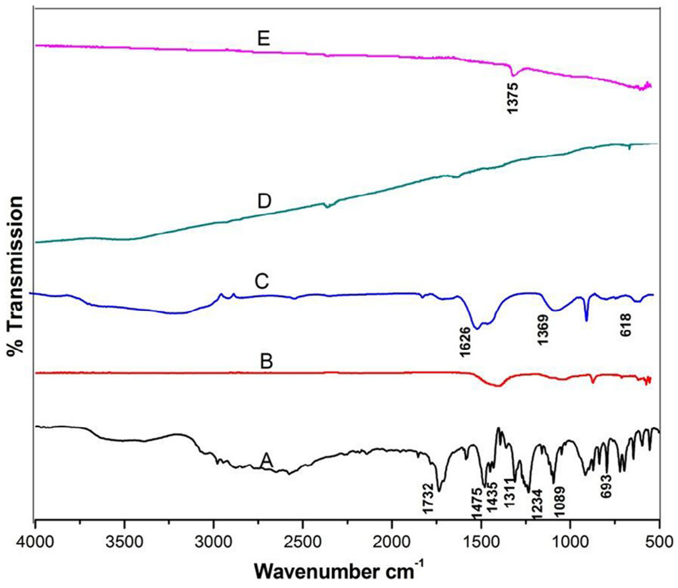


Fig. 1. FTIR spectra of 2,4-D (A), CPA before adsorption (B), CPA after adsorption (C), CPC before adsorption (D), CPC after adsorption (E).

The bands between 1100 and 1300 cm^{-1} are attributed to the presence of cellulosic derivative and CO-stretching bond [10]; similar carbonate bonds were also observed on the surface of CPC in this study.

Spectra of CPA after adsorption (Fig. 1, spectrum C) show the appearance of new bands at 1626 and 1369 cm^{-1}. This shifting of peak is due to electron donating 2,4-D surface to surface of CPA. These bands 1626 and 1369 cm^{-1}are due to the C═O vibration of the 2,4-D anion, which confirms the presence of 2,4-D in the anionic form [14].

Spectra of CPC before adsorption (Fig. 1, spectrum D) show less number of peaks, as CPC was pyrolyzed at high temperatures in inert condition. By contrast, the spectra of CPC after adsorption (Fig. 1, spectrum E) show a peak at 1375 cm^{-1}, which again confirms the presence of 2,4-D.

Elemental composition of CPA and CPC was studied using XRF technique. The XRF results are summarized in Table 2.

The elemental composition of CPA and CPC was determined by XRF analysis. Results of XRF analysis indicated that CPC has lesser oxide content than CPA because during combustion, all the carbonaceous materials in CP are completely burned to produce carbon dioxide along with oxidation of metallic content, which results in large amounts of metal oxides in CPA. During pyrolysis, however, carbonaceous materials break down to produce carbon and absence of oxygen causes lesser formation of oxides. Although weight percent composition of metal oxides identified in XRF analysis is different for the two adsorbents, the absolute elemental compositions of metals remain the same as the source is same (i.e., cotton biomass).

The XRF results of CPA show high amount of metallic oxides such as CaO (31%), K_2O (28%), and MgO (4%), which act as micronutrients for plants [24]. Biochar can be added to soil, which will greatly increase agricultural productivity due to its positive attributes noted earlier. Significant amounts of CaO (5%) and K_2O (2%) are also present in CPC. The solution pH of both samples is highly alkaline, so when added to soil, CPA and CPC will act as a neutralizer, which will improve plant growth [25]. Furthermore, biochar application as a soil amendment could contribute to carbon sequestration and renewable energy approaches. This suggests that biochar can be used as a climate change mitigation strategy [26].

High-resolution SEM images are captured for analyzing surface morphology. The surface of CPA is rough and less irregular (Fig. 2a), whereas the surface of CPC is very rough and has micropores (Fig. 2b). The small particles (micropores) on the surface of CPC are clear and distinctly visible. These micropores are responsible for adsorption of 2,4-D. Irregularities and different shapes of particles are clearly visible on the surface of CPC (Fig. 2b).

5.2. Adsorption study

5.2.1. Effect of adsorbent dosage

The effect of adsorbent dosage was studied by varying the dose of CPA and CPC from 1 to 8 g and from 0.1 to 1 g, respectively, with the concentration of adsorbate (i.e., 2, 4-D) fixed at 100 ppm. It was found that with the increase in adsorbent dose, adsorption of 2,4-D increases, which is due to the availability of more binding sites for adsorption with increase in dose. However, for the removal of 2,4-D removal becomes constant after CPA dose of 6 g. For CPC, the removal becomes constant after a dose of 0.5 g. No significant increase in adsorption was found for doses greater than the optimal dose. Therefore, 6 and 0.5 g doses were considered optimum for CPA and CPC, respectively, and these were maintained constant for all further adsorption studies. The relation between adsorbent dose and adsorption is shown in Fig. 3.

Results of XRF analysis indicated that CPC has lesser metallic oxide content as compared with CPA. During pyrolysis, however, carbonaceous materials break down to produce carbon and absence of oxygen causes lesser formation of oxides. It is well-known that adsorption efficacy depends on the chemical composition of the adsorbent. Metallic oxides such as CaO and K_2O, which in the presence of water, behave like metallic hydroxides and make the surface charge negative due to release of hydrogen. Therefore, it is very difficult to adsorb negatively charged 2,4-D anions on surface, which explains the need for

Table 2
XRF of cotton char.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3	Cl	Cr_2O_3
CPA	1.5	4.0	0.9	3.0	5.0	2.5	28.0	31.2	0.22	0.11	1.5	4.56	0.01
CPC	0.47	0.66	0.15	0.53	0.37	0.39	2.3	5.08	0.06	0.05	2.35	0.36	0.06

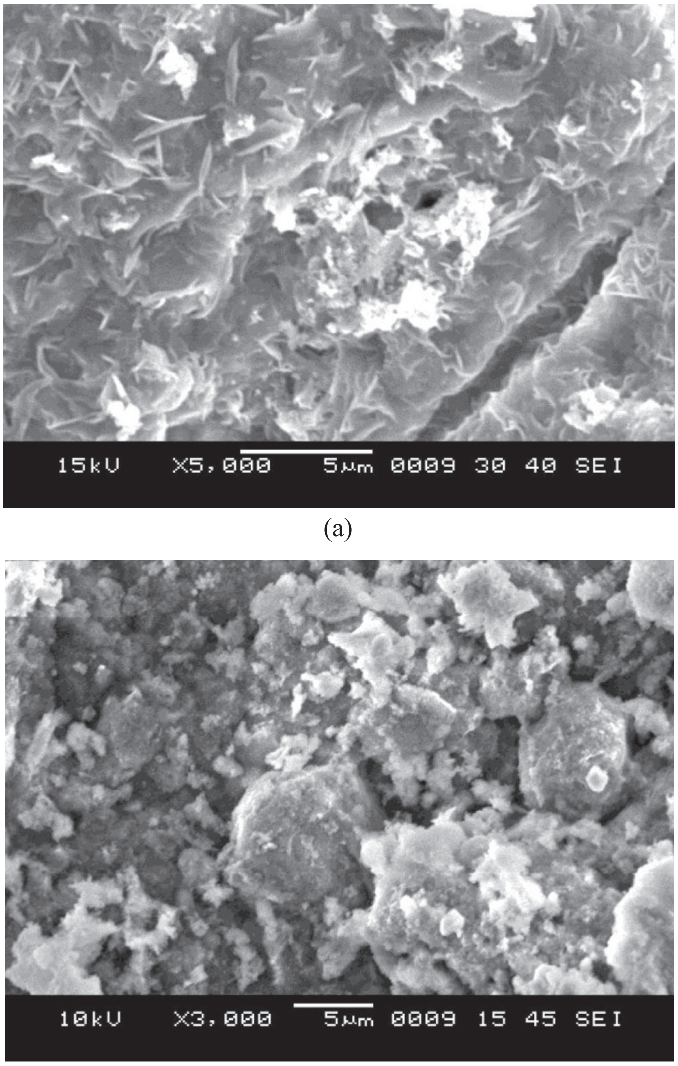


Fig. 2. (a) Scanning electron micrograph of CPA. (b) Scanning electron micrograph of CPC.

higher adsorbent dose. A previous study confirmed that 2,4-D adsorption does not occur via ligand exchange [27], but rather via electrostatic interaction. It has been found that silica is unfavorable for adsorption of anionic compounds because of its structural conformation. The surface of adsorbent is relatively more negative when the proportion of silica is higher. Thus, an adsorbent with lesser silica content is a better candidate for adsorption of anionic species such as 2,4-D. Positive centers such as Al_2O_3 also favor the adsorption of 2,4-D and compounds alike. Compared with Al_2O_3, CPA has higher silica content, and this resulted in lesser adsorption capacity of CPA. By contrast, CPC has higher amounts of organic and fixed carbon content, and thus lower optimal doses of CPC, compared with CPA, are sufficient for adsorption of 2,4-D.

5.2.2. *Effect of initial concentration of adsorbate*

The effect of different initial concentrations of solution was studied by varying the concentration of 2,4-D from 400 to 50 ppm with optimal dose of CPA and CPC, respectively. Initial variation in concentration was studied by performing batch studies, wherein optimal dose of CPA and CPC (i.e., 6 and 0.5 g) was treated with 25 ml of different concentrations of the 2, 4-D solution. The results indicated that with the increase in the initial concentration of the 2,4-D solution, the percentage removal decreases, that is, number of adsorption sites is constant and activity is limited (Fig. 4). It can be assumed that 2,4-D forms a monolayer over the CPA and CPC surface. Thus, the initial concentration curve shows a similar trend in both cases.

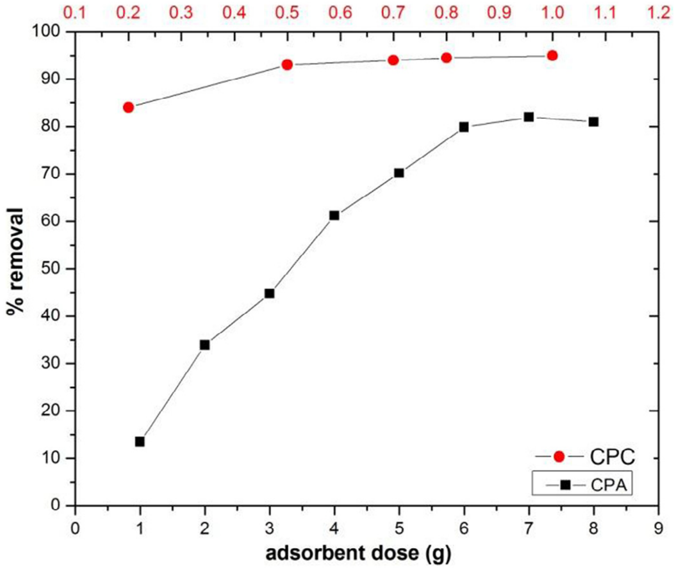


Fig. 3. Effect of adsorbent dose (CPA and CPC) on % 2,4-D removal.

5.2.3. *Effect of contact time*

The optimal dose of CPA and CPC (i.e., 6 and 0.5 g) was added to a 25 ml solution of 100 ppm concentration in different flasks and the percentage removal was reported after 3, 6, 10, 30, 60, 120, 240, 480 minutes for CPA and CPC, respectively. The

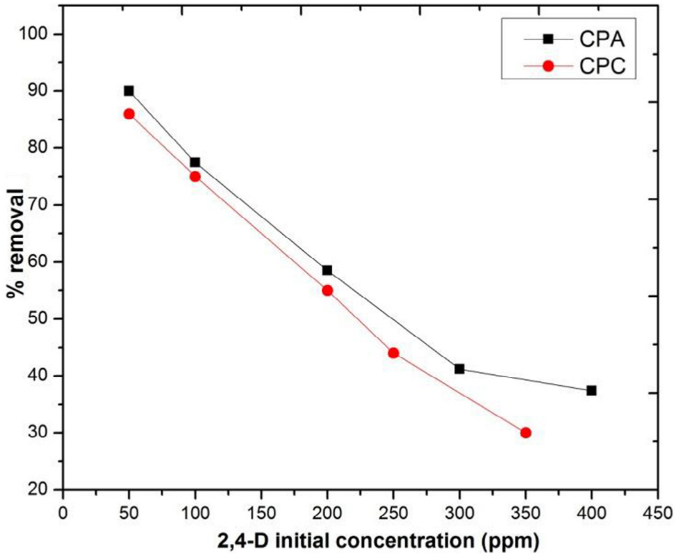


Fig. 4. Concentration study of 2, 4- D adsorption onto CPA and CPC.

Table 3
Pseudo-first-order and pseudo-second-order rate constants.

Model	Parameter	CPA	CPC
Pseudo first order	q_e,cal (mg/g)	0.37	5.36
	k_1 (min−1)	0.002	0.01
	R^2	0.105	0.96
Pseudo second order	q_e,cal(mg/g)	3.14	5.82
	k_2(g/mg/min)	0.07	0.0009
	R^2	0.99	0.99
Intra particle diffusion	k_d	0.004	0.19
	c	0.315	0.03
	R^2	0.90	0.96

equilibrium time was found to be 240 minutes in the case of CPC, whereas for CPA it was60 min (CPC > CPA). A kinetic study was performed and data obtained were fitted to the pseudo-first-order and pseudo-second-order kinetics models and intraparticle diffusion model. The pseudo-second-order model was found to show the best fit with the experimental data ($R^2 = 0.99$; Table 3). Fig. 5 shows the effect of time on the adsorption and kinetic model studies. Based on R^2 values, the pseudo-second-order model was more promising than the pseudo-first-order model. Less value of rate constant justifies slow adsorption process and more time need for attaining equilibrium.

When evaluating the effects of variation of contact time on 2,4-D adsorption, an interesting observation was that the equilibrium was achieved in a short period for CPA (60 min), compared with CPC (240 min). The order of time taken to reach equilibrium follow the trend CPC>CPA. The time difference to reach equilibrium is due to silica content of CPA (3%), which is higher than that of CPC (0.53%). As demonstrated previously, the higher silica content is responsible for faster kinetic rate is valid in this study for CPA [16].

The intraparticle diffusion model applied for experimental data (Fig. 6) demonstrated multilinearity and indicated that two consecutive steps occurred during the adsorption of 2,4-D. The first section of the curve describes the boundary layer diffusion and intraparticle diffusion of 2,4-D from the solution onto the external surface of CPA and CPC, whereas the second section of the curve describes attainment of equilibrium in which the intraparticle diffusion slows down due to non availability of adsorption sites on the surface of CPA and CPC.

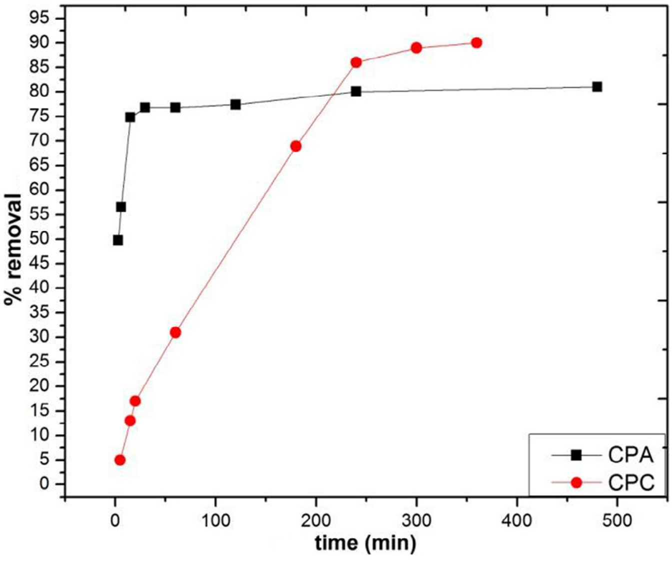


Fig. 5. Effect of contact time (CPA and CPC) on the removal of 2,4-D.

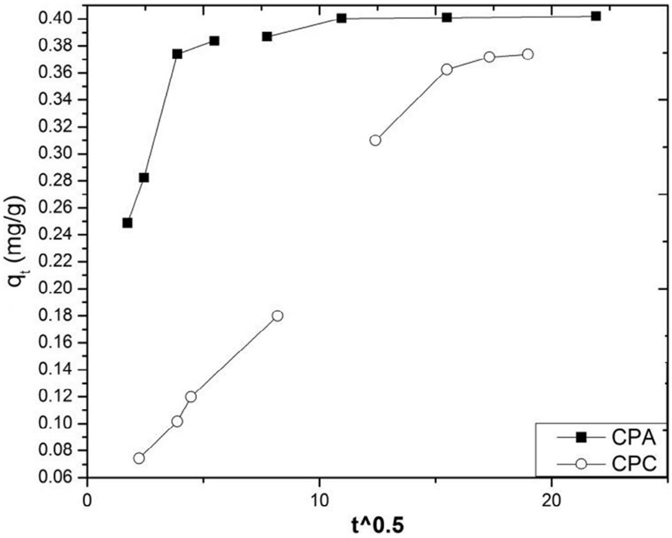


Fig. 6. Plot for intra-particle diffusion of 2,4-D onto CPA and CPC.

5.2.4. Adsorption isotherms

Adsorption isotherm illustrates the specific relationship between the adsorbate molecules and the adsorbent. Langmuir and Freundlich adsorption models were studied and their parameters are tabulated below Table 4. R^2 values show that Langmuir model fits well than Freundlich with highest adsorption capacity (q_0) of 3.93 mg/g for CPC and 0.64 mg/g for CPA. This difference is due to the carbon content and high surface area of CPC.

Langmuir isotherm assumes equal affinity of all sorbent sites toward the sorbate molecules; adsorbed layer is one monolayer thick and no lateral interaction between adsorbed, adjacent sorbate molecules [28]. This implies favorability of Langmuir isotherm as $0 < B < 1$, here RL which is Langmuir constant generally is written as B. If the value of B is less than 1 Langmuir isotherm is favorable. Freundlich adsorption isotherm was also

Table 4
Langmuir and Freundlich isotherm parameters.

Isotherm	Parameters	CPA	CPC
Langmuir	q_0	0.64	3.93
	B	0.042	0.004
	R^2	0.98	0.99
	ND	1.21	2.32
	NSD	2.48	3.47
Freundlich	K_f	0.38	1.47
	n	3.15	8.62
	R^2	0.94	0.43
	ND	6.42	19.5
	NSD	14.38	35.64

applied to the experimental data to describe adsorption of 2,4-D over CPA and CPC. Isotherm assumes heterogeneous, reversible and non ideal adsorption processes [29]. However Freundlich adsorption isotherm fits the experimental data with poor correlation ($R^2 > 0.95$ and 0.43 for CPA and CPC and the R^2 values are less than that those of Langmuir adsorption isotherm.

6. Conclusion

This study demonstrates that ash and char derived from cotton plant can be used as cheap adsorbents for the removal of 2,4-D. The XRF result of CPA indicated the presence of CaO and K_2O whose addition will contribute to the growth of plants by acting as a source of micronutrients. By contrast, CPC contains fewer amounts of CaO and K_2O. CHNS analysis of CPC results into high amount of organic carbon, which can be added to soil for carbon enrichment. The SEM image indicates that the surface of CPC is highly rough and irregular, which favors the adsorption of 2,4-D onto its surface. FTIR spectra confirm the presence of 2,4-D on the surface of both CPA and CPC. The BET surface area was found to be 2 and 109 m^2/g for CPA and CPC, respectively. Langmuir adsorption capacity was found to be 0.64 mg/g for CPA and 3.93 mg/g for CPC. From the aforementioned results, it can be concluded that CPC is a good adsorbent of 2,4-D while CPA acts as a source of micronutrient to the soil. Adsorption study data well fitted with the Langmuir isotherm and pseudo-second-order kinetics in both cases.

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Abbreviations

CPC	cotton plant char
2,4-D	2,4-dichlorophenoxyacetic acid
SEM	scanning electron microscope
CHNS	carbon, hydrogen, nitrogen, sulfur
BET	Brunauer–Emmett–Teller N_2 adsorption technique for surface area [m^2/g]
XRF	X-ray fluorescence technique
q_t	concentration at time t [mg/g]
q_e	concentration at equilibrium time [mg/g]
c_0	initial concentration of adsorbate [mg/L]
c_e	equilibrium concentration of adsorbate in solution [mg/L]
v	volume of solution in liters [L]
w	mass of dry adsorbent[g]
q_e	adsorption capacity of adsorbate at equilibrium [mg/g]
k_1	pseudo first-order rate constant [1/h]
k_2	rate constant of pseudo-second-order model [g/mg/minute]
R	correlation coefficient
q_0	Langmuir capacity [mg/g]
B	Langmuir constant [L/mg]
K_F	Freundlich isotherm constant related to adsorption capacity [[mg/g] [L/mg]1/n]
n	Freundlich isotherm constant related to adsorption intensity

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