Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28953

276 (2022) 271–281
November

Feasibility study on the utilization of low-cost sawdust for adsorption of caffeine: equilibrium, optimization, and response surface modeling

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Received 3 May 2022; Accepted 22 September 2022

ABSTRACT

The study focuses on the adsorption of caffeine (CAF) from aqueous solutions onto sawdust (SD), a naturally available, eco-friendly, and low-cost adsorbent. The influence of various operating parameters such as; CAF initial concentration (5–20 mg/L), SD dosage (0.5–3.0 g/L), and pH (3.0–9.0) was investigated in detail. The experimental results of the adsorption process showed the maximum CAF removal efficiency of 94.5% at optimized conditions (CAF initial concentration 5 mg/L, SD dosage 2.0 g/L, and pH 7.0). The applicability of adsorption isotherm models for CAF removal by SD has also been revealed. The R^2 values obtained for Langmuir and Freundlich isotherms (0.9371 and 0.9966) showed that the Freundlich isotherm model with the higher R^2 value of 0.9966 had better suitability than the Langmuir isotherm model. The suitability of experimental data was analyzed with response surface methodology using Design-Expert software. The obtained analysis of variance results with a coefficient of determination; R^2 = 0.9643 and adjusted R^2 value = 0.9516 demonstrated good agreement between experimental and predicted data. The 3D surface plots confirm the significance of all the three parameters investigated.

Keywords: Caffeine; Sawdust; Adsorption; Langmuir isotherm; Freundlich isotherm

1. Introduction

Caffeine (CAF) is one of the pharmaceutical compounds, the most consumed psychoactive drug all over the world [1], an emerging contaminant (EC) [2,3], and a stimulant that is found in hundreds of drugs from analgesics and cold medicines. It is an alkaloid used as a cardiac, cerebral, and respiratory stimulant. CAF also can be employed as an additive in drugs for analgesic effects. It is found in tea, coffee, soft drinks, and chocolates [4,5] and its average consumption per person is around 200 mg/d [6]. A typical 237 mL cup of coffee contains 95–165 mg of CAF. Similarly, a cup of black cola soda contains 24–46 mg of CAF.

CAF has high water solubility (K_s > 10,000 mg/L), low octanol-water partition coefficient ($\log K_{ow}$ = –0.07) and insignificant volatility [7]. However, intense usage of CAF over the long term can lead to irritability, mutation effects such as inhibition of DNA, anxiety, tremors [8], and cardiovascular diseases [9,10]. Chronic exposure to CAF causes headaches, migraine, and changes in cell cycle control functions [11].

CAF is identified as a micropollutant and has been detected in freshwater, marine systems, coastal waters, and wastewaters with concentrations ranging from ng/L to μg/L [5,12,13] the concentrations of which are adequate to meet the values of the toxicity threshold of aquatic biota [14]. Previous studies revealed that an average of 3 kg of CAF are thrown away every day into the Pacific Ocean which causes acidification of the oceans [12]. Short-term exposure to CAF is not harmful to aquatic living organisms [15]. However, the toxicological effects of CAF over the long-term release into water bodies may cause sublethal effects

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on the aquatic living organisms such as oxidative stress and lipid peroxidation in *Diopatra neapolitana* and *Arenicola marina* [7,16,17]. In addition, when the concentration of CAF exceeds 30 mg/L, it may create coral bleaching and inhibitory effects on algae growth [18].

The conventional wastewater treatment methods that include physical (filtration, adsorption), chemical (coagulation and electrolysis), and biological (activated sludge treatment) are found to be inefficient for the removal of organic compounds [19]. This led the researchers to focus more on innovating new treatment methods for the removal of organic compounds. Emerging new technologies such as membrane bioreactors [20] and advanced oxidation processes [21] were found to be successful in degrading these compounds. However, adsorption processes using activated carbon (AC) are the most widely used methods [22].

Adsorption is one of the most effective widely used water treatment methods to reduce hazardous pollutants present in aqueous solutions. Conventional activated carbon (AC) is the preferred adsorbent but it is limited due to its relatively high cost and requirement for regeneration [23,24]. In recent years, researchers started focussing on developing low-cost adsorbents using various precursors such as clays, zeolites, biosorbents, agricultural solid waste, industrial by-products, etc. [25–29].

The lignocellulosic materials are the most common precursor materials to obtain AC [24]. The selection criteria for the precursor are; (i) It should be easily available, (ii) low-cost, and (iii) its abundance. The sawdust (SD) as a lignocellulosic material, is freely available, and abundant up to 24.15 million m^3/y worldwide [30,31] and can replace AC as a good precursor.

Sawdust plays a prominent role in the removal of water contaminants by adsorption because it contains functional groups such as carboxyl, hydroxyl, phenolic, and amide groups in its structure [32]. It could be modified by alkali or acid to increase its adsorption properties. More literature is available on the composition and methods of preparation of sawdust as an efficient adsorbent [33–36]. SD materials were employed for biosorption and found to be very much efficient [37] due to the fact that these materials were employed as adsorbents without any pre-treatment and could replace activated carbon as an adsorbent material. SD materials are waste products obtained from the wood industry, abundantly available, and cost less or no cost. Many of the studies have utilized SD as an adsorbent for the degradation of dyes. Limited studies had employed SD for the adsorption studies of pharmaceutical compounds among which CAF is one compound.

Therefore, the main objective of this work was to perform and demonstrate the adsorption potential of locally available low-cost sawdust obtained from the industry as a mixture of different types of wood through batch studies. CAF was chosen as a model pharmaceutical compound because it is typically labeled as a tracer species for pharmaceuticals [38,39]. The effect of various operating parameters such as; CAF initial concentrations, SD dosage, and pH on CAF adsorption was evaluated and the parameters were optimized. To describe the CAF adsorption isotherms, Langmuir and Freundlich models were employed. The suitability of experimental data was investigated with response surface methodology using Design-Expert software.

2. Materials and methods

2.1. Materials

The adsorbent SD was obtained from a local wood processing industry and was a mixture of various types of wood. CAF (≥99% analytical grade, molecular formula – $C_8H_{10}N_4O_2$; mol.wt. – 194.19 g/mol) was purchased from Sigma-Aldrich. Other reagents hydrochloric acid (36.5%–38.0%, CAS No. 7647-01-0) and sodium hydroxide (99%, CAS No. 88-12-0), dichloromethane, acetonitrile, and hexane were of high-performance liquid chromatography grade purchased from Merck. Double-distilled water (Merck) was used for analysis. The reaction mixture was prepared by adding the required concentrations of CAF in distilled water. The pH of the reaction mixture was adjusted by 0.1 M NaOH and 0.1 M HCl. The key physico-chemical characteristics of CAF are presented in Table 1.

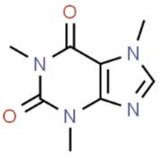
2.2. Preparation of adsorbent

The SD used in this study was collected from five local sawmills and was a mixture of various wood. The obtained SD was homogeneously mixed and continuously boiled with distilled water till it becomes colorless or a clear solution appears. After that, it was dried at the temperature of 60°C for 2 d [40,41]. The dried SD was pulverized, powdered, and sieved through a 300–500 µm sieve. The SD passing through a 500 µm sieve and retained in a 300 µm sieve was stored in glass bottles and used in this study.

2.3. Adsorbent characterization

Fourier-transform infrared spectroscopy (FTIR) was performed using a spectrophotometer Shimadzu/IRPrestige-21 through the KBr method. Spectra were obtained in the range of 4,000 to 400 cm^{-1} with a transmittance of 50 scans. The surface morphology of SD was analyzed by the scanning electron microscope (SEM) Shimadzu SSX-550 model.

Table 1
Key physico-chemical characteristics of CAF

Parameters	Values
Structure	
Molecular weight	194.19 g/mol
Molecular formula	$C_8H_{10}N_4O_2$
pKa	14 (25°C)
logK_{ow}	–0.07
Water solubility	21,600 mg/L
Density	1.23 g/cm^3

2.4. Preparation of adsorbate

The stock solution of CAF was prepared by dissolving 1.0 g of CAF in double-distilled water in a 1 litre volumetric flask in order to obtain a concentration of 1 g/L. The working solution was prepared by diluting the CAF stock solution in accurate proportions to the required initial concentrations of 5–20 mg/L and was used to plot the calibration curve. The calibration curve is shown in Fig. 1. Ganzenko et al. [42] quantified the CAF concentration in pharmaceutical wastewater as 19.4 mg/L. Subedi et al. [43] and Li et al. [44] quantified CAF concentrations in Indian wastewater as 61 and 30 µg/L, respectively. Based on the previous studies conducted by various researchers, the concentration range of CAF in this study was selected.

2.5. Adsorption studies and isotherms

The adsorbent sawdust was triturated and sieved in order to obtain particles with medium diameter. The stock solution of CAF (1,000 mg/L) was prepared by dissolving the analytical standard in water which was used to prepare all the work solutions by required dilution. Quantification of CAF was performed using an INFRA DIGI IR513C Digital Single Beam UV-VIS Spectrophotometer (Gaurav Scientific & Chemical, Raipur, India) with absorbance measurements at 273 nm. The calibration curve was plotted with concentrations ranging from 5.0–20.0 mg/L and used to determine the absorbate concentration after all adsorption assays. The CAF removal efficiency was calculated using Eq. (1).

$$\text{CAF Removal}(\%) = \frac{\text{CAF Initial concentration} - \text{CAF Final Concentration}}{\text{CAF Initial concentration}} \times 100 \tag{1}$$

All glassware used in these experiments was washed with methanol, deionized water, and acetone and then dried at 110°C for 3 h. The repeatability of the measurements was verified by the standard deviation (σ) and coefficient of variation (CV). The error in measurement for all samples was estimated to be within ±5%.

Adsorption experiments were conducted by adding 2.0 g of SD in 1,000 mL, that is, in beakers having a volume of 1,000 and 500 mL distilled water was taken and 1 g SD was added. In the beakers having 500 mL volume of working solution with 2.0 g/L concentration of SD, each different initial concentrations of CAF; 5, 8, 10, 12, 15, and 20 mg/L were added and kept in the Jar test apparatus. The sample was agitated at 150 rpm for 180 min to attain equilibrium. The sample was left undisturbed for 2 min for the settling of adsorbent particles. The concentrations of CAF were measured in UV-VIS Spectrophotometer at 273 nm. The amount of adsorption at time t, q_t (mg/g) was calculated from Eq. (2):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

where C_o: liquid-phase initial concentration of CAF in mg/L, C_t: liquid phase remaining concentration of the CAF in mg/L, V: volume of the solution in L and W: mass of dry adsorbent in g.

The amount of adsorption at equilibrium q_e (mg/g) was calculated using Eq. (3):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{3}$$

where C_e: remaining liquid-phase concentration of the CAF in mg/L at equilibrium.

The CAF removal was calculated using Eq. (4):

$$\text{CAF Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{4}$$

The Langmuir and Freundlich isotherm models were chosen to analyze the data. The Langmuir and Freundlich models were described by Eqs. (5) and (6).

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max}} \times \frac{1}{C_e} + \frac{1}{q_{\max}} \tag{5}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{6}$$

where $q_{\max}$ (mg/g) is the maximum adsorption, K_L (L/g) is the Langmuir equilibrium constant, K_f (L/g) is the Freundlich constant or relative sorption capacity, and n is a constant indicating adsorption intensity [39,45–48]. Data were modeled in a linear form and the correlation coefficients were obtained.

2.6. Data analysis

The CAF adsorption was optimized using response surface methodology (RSM) based on central composite design (CCD). The three factors; feed solution pH, initial CAF concentration, and SD dosage were assessed for the response CAF removal for 180 min at every 30 min interval. The experimental data were analyzed using Design-Expert software Version 7.0.0 Stat-Ease [49].

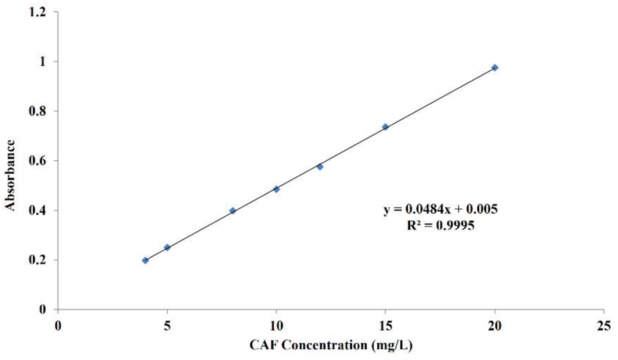


Fig. 1. Standard curve of CAF at a concentration range from 0 to 20 mg/L at room temperature.

3. Results and discussion

3.1. Characteristics of adsorbent

FTIR spectrum was obtained from 4,000 to 400 cm^{-1} range for SD and is shown in Fig. 2a. The bandwidth between 3,300 to 3,700 cm^{-1} with a peak around 3,344 cm^{-1} indicates the presence of hydroxyl (OH^-) groups and the chemisorption of water on the carbon surface [50,51]. Furthermore, the lower peaks evidenced in 2,987; 2,861; 1,438 and 458 cm^{-1} could be due to the presence of aliphatic groups such as alkanes corresponding to C–H bonds [50,52]. The band referred to in the region between 1,660 and 1,662 cm^{-1} is due to the presence of carboxyl, carbonyl, and aromatic carbon radicals which have C=C and C=O links. The bands in 1,437 cm^{-1} and between 1,112 and 1,223 cm^{-1} are characteristics of phenolic and lactam groups [52–54].

SEM images at different magnifications are shown in Fig. 2b and c. The adsorbent material SD has an irregular surface with the presence of pores, swellings, and canals. These characteristics are favorable for adsorption since the interaction between liquid and solid may occur both internally and externally [55].

3.2. Effect of pH on CAF removal

The solution pH is an important parameter that influences the adsorption behavior. The effect of solution pH on CAF removal was studied by varying the solution pH from 3.0–9.0 using 0.1 M NaOH and 0.1 M HCl. For different pH, a 500 mL sample containing 5 mg/L of CAF and 2.0 g/L of SD was agitated at 150 rpm for 180 min in order to attain equilibrium. Continuous mixing was provided with a constant agitation speed of 180 rpm for better mass transfer with a high interfacial area of contact. Agitation speed influences the distribution of solute in the bulk solution and the formation of external boundary film. Agitation also increases the external mass transfer coefficient resulting in quicker adsorption of CAF molecules.

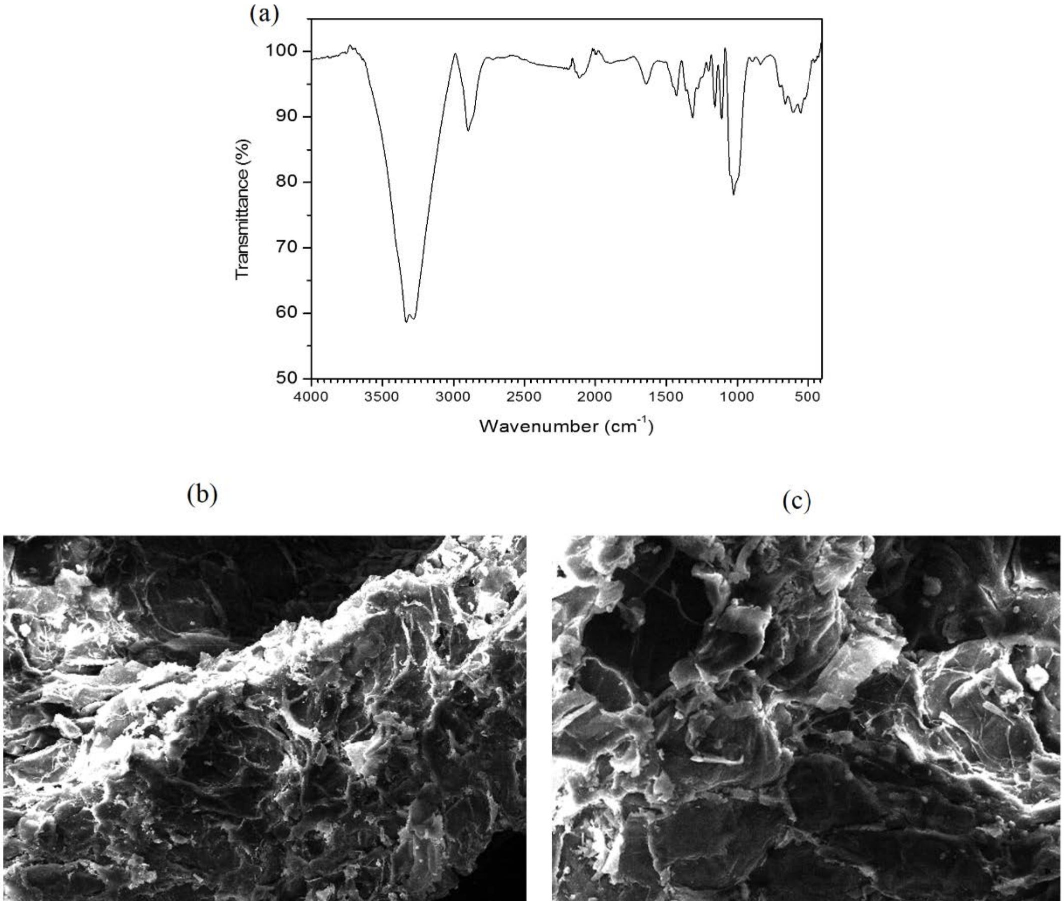


Fig. 2. (a) FTIR and (b,c) SEM images of sawdust surface.

By varying pH, the surface charge and degree of ionization of an adsorbent can be affected. In order to understand the adsorption mechanism, it is very much essential to determine the point of zero charges (pH_{pzc}) at which the surface charge of SD is zero. The pH_{pzc} value of SD (6.4) is closer to the neutral value. The pH_{pzc} value indicates the type of active sites and the adsorption ability of adsorbents. Cationic compound adsorption is enhanced at $pH > pH_{pzc}$ owing to the presence of OH^- and COO^- groups. Meanwhile, anionic compound adsorption is favored at $pH < pH_{pzc}$ at which the surface is positively charged.

An important parameter that determines the interaction between adsorbents and adsorbates is the reaction solution pH. Fig. 3a illustrates the effect of solution pH on CAF removal efficiency. When the pH of the solution is changed, it exhibits changes in the surface charges of SD and influences the protonation of the functional group present on the surface of materials. It can be seen from the graph that the maximum CAF removal efficiency of 94.5% was obtained at pH = 7. The CAF removal efficiency decreased significantly after pH 7.0 and reached the minimum value of 83.2% at pH 9.0. From pH 3.0–7.0, there is a predominance of CAF neutral form and the negative surface of SD resulted in higher removal efficiencies. This can be attributed to π–π interactions and hydrogen bonds between CAF heterocyclic rings and SD aromatic rings [56]. On the other hand, the increase in solution pH led to a decrease in removal efficiencies which can be attributed to an increase of CAF^- species in solution. This may be due to the repulsion between CAF^- molecules and the negative surface of SD. Similar observations were made by Islam et al. [57] and Ozacar and Sengil [58] for dye removal employing activated carbon (AC) and sawdust (SD) as adsorbents. The results obtained in this study could be comparable with the results of a few recent studies for CAF removal and are presented in Table 2.

3.3. Effect of adsorbent dose on CAF removal

The effect of adsorbent dosage on CAF removal was studied by varying the concentration of adsorbent from 0.5–3.0 g/L with a constant initial CAF concentration of 5 mg/L at a sample pH of 7.0 and agitating the reaction mixture in the Jar test apparatus for 180 min (in order to achieve equilibrium) at 150 rpm. The reaction mixture was left undisturbed for 30 min in order to favor the complete settling of adsorbent particles.

Fig. 3b demonstrates the effect of SD dosage on CAF removal efficiency. The percentage removal of CAF increased from 64.3%–94.5% with an increase in adsorbent dose from 0.5–2.0 g/L. Further increase in SD dosage to 3.0 g/L, decreased the CAF removal to 88.2%. The increase in percentage removal was due to an increase in available adsorption surfaces and the availability of more adsorption sites. The increase in adsorption with adsorbent dosage (from 0.5–2.0 g/L) can be attributed to an increase in the adsorption surface and the availability of more adsorption sites [62,63]. Further increase in adsorbent dosage (after 2.0 g/L) resulted in a decrease in CAF removal. However, if the adsorption capacity of the SD was expressed in mg/g of material, the capacity decreased with increasing the amount of SD. This could be due to overlapping or aggregation of adsorption sites resulting in a decrease in total

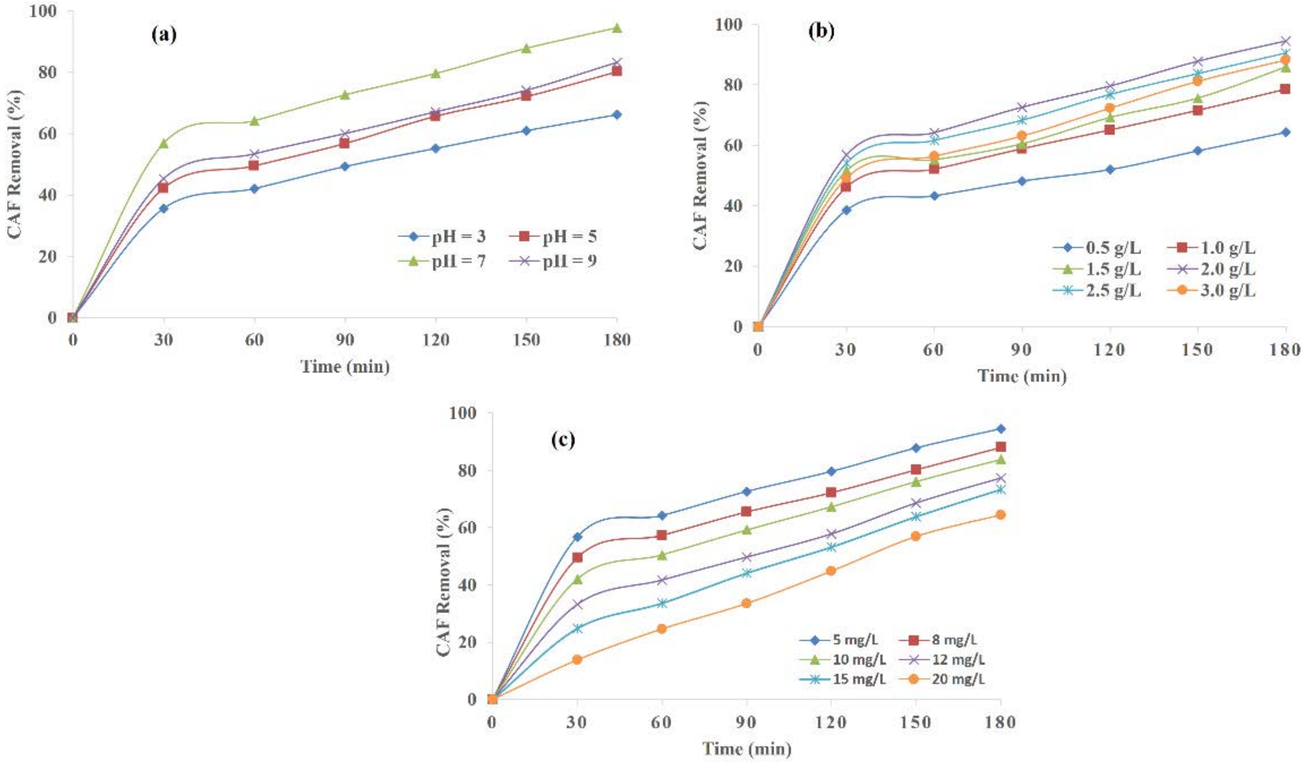


Fig. 3. Effect of (a) solution pH (3.0–9.0), (b) SD dosage (0.5–3.0 g/L) and (c) initial CAF concentrations (5.0–20.0 mg/L) on CAF removal.

adsorption surface area available for CAF and an increase in the diffusion path length. Similar results were observed by Etim et al. [63] for cationic dye removal using coconut coir dust in which the authors observed an increase in removal efficiency from 92.1%–99.5% while increasing the adsorbent dosage from 0.05–0.20 g/L.

3.4. Effect of CAF initial concentrations on its removal

The percentage removal of CAF depends upon the initial amount of CAF concentration. The effect of initial CAF concentration depends on the immediate relation between the CAF concentration and the available binding sites on the adsorbent surface. The decrease in CAF removal with an increase in CAF initial concentration may be due to the saturation of adsorption sites on the adsorbent surface [64] and the adsorbent capacity increased with an increase in the initial concentration of CAF. When the initial CAF concentration is lower, there are unoccupied active sites on the adsorbent surface and when the initial CAF concentration increases, the active sites required for adsorption of the CAF molecules may not be available [65].

The percentage adsorption decreased with an increase in the CAF initial concentration and increased as the contact time prolonged. However, the increase in the initial CAF concentration caused an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial CAF concentration [66]. In other words, for higher initial CAF concentration, the residual CAF concentration of CAF molecules will be higher, the ratio of the initial number of CAF molecules to the available adsorption sites is low and subsequently, the fractional adsorption becomes independent of the initial concentration.

Fig. 3c depicts the adsorption of CAF. The adsorption of CAF was 99.5% maximum at a lower initial concentration of CAF (5 mg/L) as compared to higher initial concentrations. The lower removal efficiencies obtained at higher initial concentrations may be due to the high driving force created by the high CAF concentration to overcome all mass transfer resistance of the CAF between the aqueous and solid phases [67].

3.5. Langmuir and Freundlich adsorption equilibrium models

In this study, the equilibrium data for CAF on SD were analysed and fitted with Langmuir and Freundlich isotherms at different initial concentrations of CAF. The Langmuir isotherm model is a monolayer model and is based on the assumption that all sites should have an equal affinity towards the adsorbate. Each molecule adsorbed on the surface has the same adsorption activation energy and hence forms a monolayer [32,68]. In Langmuir isotherm, the quantity R_L is taken to be the relative velocity in vapour-liquid equilibrium. For a favourable system, R_L lies between 0 and 1 for each of the different concentrations of CAF. R_L is larger than zero for an unfavourable system [31]. The separation factor $R_L = 0.0726$ and $0 < R_L < 1$ obtained in this study indicates favourable adsorption.

The Langmuir and Freundlich isotherm constants are shown in Table 3. Unlike the Langmuir isotherm model, the Freundlich isotherm model is restricted to monolayer formation. It considers that the adsorption surface is heterogeneous and has unequal available sites with different energies of adsorption. From Fig. 4a and b, it was found that the adsorption equilibrium data fitted both Langmuir and Freundlich isotherms with correlation coefficient values of 0.9371 and 0.9966 for Langmuir and Freundlich isotherms respectively. The obtained experimental data fitted more closely with the Freundlich isotherm (Fig. 4b) confirms the heterogeneous coverage of CAF with SD particles. The value of n greater than unity ($n = 3.25$) obtained in the Freundlich isotherm indicates that CAF is significantly adsorbed on SD. The results obtained in this study could be comparable with the results of others [69–71]. Ngeno et al. [69] investigated the removal of CAF using water hyacinth biochar as an adsorbent and reported $R^2 = 0.990$, $n = 2.101$ and $K_f = 1.064$ (mg/g) for Freundlich and $R^2 = 0.965$, $q_{\max}$ (mg/g) = 2.488, $K_L = 0.901$ (L/mg), $R_L = 0.0999$ for Langmuir isotherms respectively. Similarly, Beltrame et al. [70] investigated the CAF removal using activated carbon prepared from pineapple plant leaves as an adsorbent and reported

Table 3
Langmuir and Freundlich isotherm constants

Isotherm	Intercept	Slope	R^2	Other parameters
Langmuir	0.35791	0.1403	0.9371	$q_{\max}$ (mg/g) = 2.79, $K_L = 2.555$ (L/mg), $R_L = 0.0726$
Freundlich	0.2475	0.3078	0.9966	$1/n = 0.3078$, $n = 3.25$, $K_f = 1.7681$ (mg/g)

Table 2
Comparison of results with recent literature

Adsorbent	Maximum adsorptive capacity (mg/g)	Optimized parameters	CAF removal efficiency (%)	References
Grape stalk activated carbon (GSAC)	19.575	[GSAC] = 3.0 g/L, [CAF] = 20 mg/L, pH = 4.0, contact time = 60 min	95.8	[59]
Acacia mangium wood activated carbon (OAMW-AC)	30.3	[OAMW-AC] = 3.0 g/L, [CAF] = 10 mg/L, pH = 7.7, time = 60 min	93	[60]
Guineenis endocarp activated carbon	13.582	[Adsorbent] = 0.20 g/L, [CAF] = 20 mg/L, pH = 2.0, time = 300 min	95.8	[61]

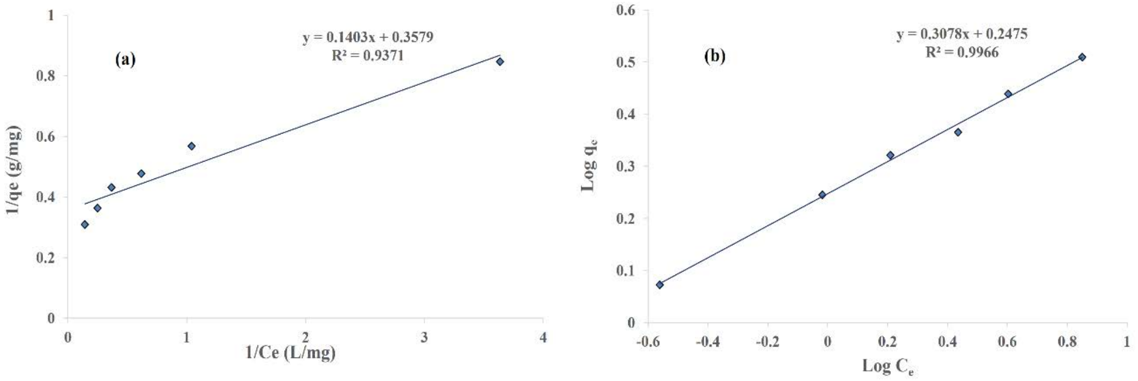


Fig. 4. (a) Langmuir and (b) Freundlich isotherm plots for CAF adsorption onto sawdust.

$R^2 = 0.8852$, $n = 4.46$ and $K_f = 44.37$ (mg/g) for Freundlich and $R^2 = 0.9871$, $q_{\max}$ (mg/g) = 155.50, $K_L = 0.901$ (L/mg), $R_L = 0.088$ for Langmuir isotherms respectively. Lenzi et al. [71] investigated CAF adsorption on bentonite clay and reported $R^2 = 0.7928$, $n = 2.8050$ and $K_f = 18.5097$ (mg/g) for Freundlich and $R^2 = 0.9671$, $q_{\max}$ (mg/g) = 41.667, $K_L = 0.7186$ (L/mg), $R_L = 0.0651$ for Langmuir isotherms respectively.

3.6. RSM modelling for optimization of operational parameters

The effects of selected independent process variables were evaluated by the RSM. Single and synergetic effects of three variables; x_1 adsorbent dosage (g/L), x_2 CAF initial concentration (mg/L), and x_3 pH were evaluated at 2 levels with Y CAF removal as a response.

Parameters used in the central composite design were; adsorbent dosage, CAF initial concentration, and pH. The parameters used in the central composite design (CCD) are presented in Table 4.

The experimental design based on CCD is presented in Table 5. Based on the experimental data and CCD matrix a second-order polynomial expression was obtained and the expression is:

$$\text{CAF Removal}(\%) = -31.26596 - 1.93538x_1 + 42.21424x_2 - 24.82764x_3 - 9.37451x_2^2 - 1.78341x_3^2 \quad (7)$$

The positive sign in the expression represents the synergetic effects while the negative sign indicates the antagonistic effects. Analysis of variance (ANOVA) was used to test the significance and adequacy of the model. The results of the ANOVA quadratic model for CAF removal are presented in Table 6. The graphical illustrations of residuals vs. predicted, residuals vs. run, Box–Cox plot for power transforms, and residuals vs CAF concentrations for adsorption on SD are presented in Fig. 5. Fig. 6a–c are the graphical representations of the normal plot of residuals, predicted vs. actual, and RSM 3D surface plots for CAF adsorption on the SD surface. The large 'Model *F*-value' of 75.68 and 'Prob. > *F*' less than 0.0500 indicate that the

Table 4
Parameters used in central composite design (CCD) for CAF adsorption

Parameter	Symbol	Low (–1)	Centre (0)	High (+1)
x_1	CAF concentrations (mg/L)	5	10	20
x_2	SD dosage (g/L)	0.5	1.5	2.5
x_3	pH	3.0	6.0	9.0

Table 5
Experimental data in the central composite design for the study of the adsorption of CAF

Run	Factor 1 x_1: CAF concentration (mg/L)	Factor 2 x_2: Catalyst dosage (g/L)	Factor 3 x_3: pH	Response 1 CAF removal (%)
1	5.00	2.00	7.00	94.5
2	8.00	2.00	7.00	88.0
3	10.00	2.00	7.00	83.8
4	12.00	2.00	7.00	77.3
5	15.00	2.00	7.00	73.3
6	20.00	2.00	7.00	64.4
7	5.00	0.50	7.00	64.3
8	5.00	1.00	7.00	78.6
9	5.00	1.50	7.00	85.9
10	5.00	2.00	7.00	94.5
11	5.00	2.50	7.00	90.5
12	5.00	3.00	7.00	88.2
13	5.00	2.00	3.00	66.2
14	5.00	2.00	5.00	80.2
15	5.00	2.00	7.00	94.5
16	5.00	2.00	9.00	83.2
17	17.00	2.00	7.00	68.5
18	7.00	2.00	7.00	90
19	9.00	2.00	7.00	85.3
20	13.00	2.00	7.00	75.1

Table 6
ANOVA results for CAF removal efficiency

Source	Sum of squares	df	Mean square	F	p	
Model	1,847.61	5	369.52	75.68	<0.0001	Significant
x_1: CAF concentration	1,257.82	1	1,257.82	257.61	<0.0001	
x_2: SD dosage	780.33	1	780.33	159.82	<0.0001	
x_3: pH	252.35	1	252.35	51.68	<0.0001	
x_2^2	307.25	1	307.25	62.93	<0.0001	
x_3^2	311.57	1	311.57	63.81	<0.0001	
Residual	68.36	14	4.88			
Lack of fit	68.36	12	5.70			Not significant
Pure error	0.000	2	0.0000			
Cor. total	1,915.97	19				

Std. Dev. = 2.21; Mean = 81.31; C.V.% = 2.72; PRESS = 1067.3; Adeq. Precision = 23.999.

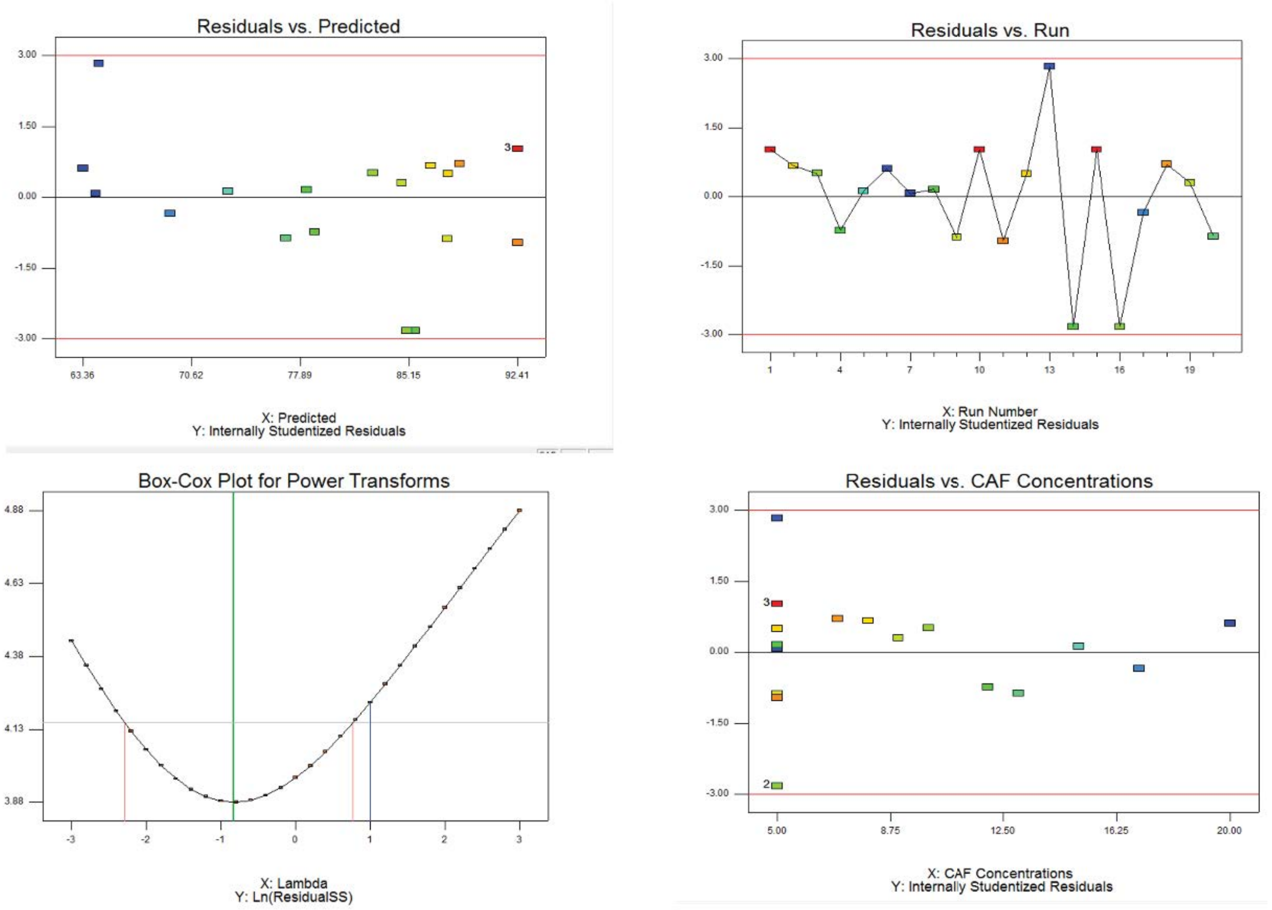


Fig. 5. (a) Residuals vs. predicted, (b) residuals vs. run, (c) Box–Cox plot for power transforms, and (d) residuals vs. CAF concentrations for adsorption on SD.

model terms are significant and there is only a 0.01% chance that a 'Model F-value' this large could occur due to noise. The model terms x_1, x_2, x_3, x_2^2, and x_3^2 are significant for CAF removal response. Furthermore, the 'Adeq. Precision' value 23.999 > 4 also confirms the adequacy of the model. The R^2 value (0.9643) and 'Adjusted R^2' value (0.9516) indicates a good correlation between the predicted values and the experimental data and hence the data fitted well with the range studied. This has been confirmed with the plot of predicted vs. actual response (Fig. 6b). The residuals falling on the straight line confirm the normal distribution of errors.

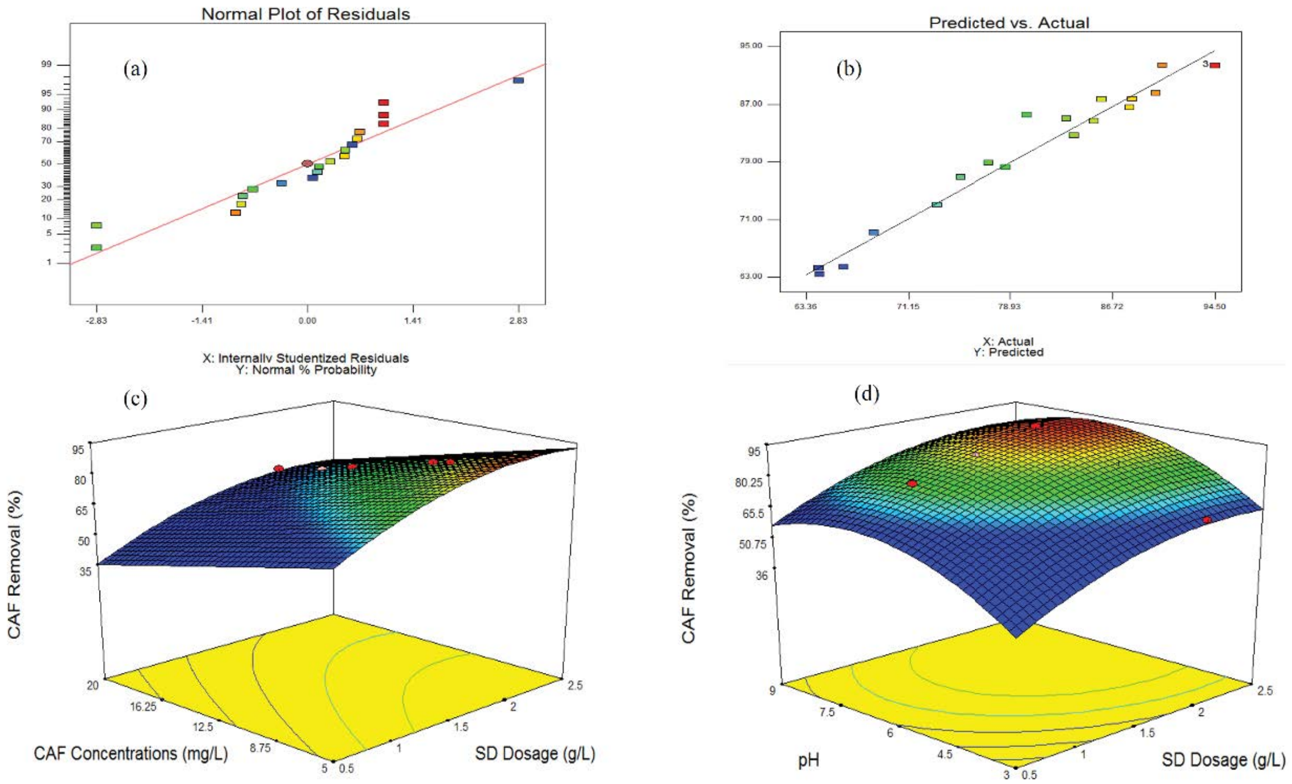


Fig. 6. (a) Normal plot of residuals, (b) predicted vs. actual and (c) response surface methodology 3D surface plots for CAF adsorption on SD.

The three-dimensional response surface plots are shown in Fig. 6. Fig. 6c and d are the graphical representations of equation (7). CAF removal increases with the decrease of CAF initial concentration. CAF removal was maximum at pH 7.0. Fig. 6c illustrates the effect of CAF initial concentration and SD dosage on CAF removal. Similarly, Fig. 6d demonstrates the influence of pH and mass adsorbent dosage on CAF removal. CAF removal increases with an increase of pH and SD dosage up to a certain extent and decreases. The maximum CAF removal was obtained at pH 7.0 and an SD dosage of 2.0 g/L.

4. Conclusions

The present study demonstrated the feasibility of employing low-cost SD obtained from the industry as a mixture for CAF removal in aqueous solutions. The maximum CAF removal efficiency of 94.5% was obtained at optimum conditions (CAF concentration – 5 mg/L, SD dosage – 2.0 mg/L and pH – 7.0). The adsorption process followed Langmuir and Freundlich isotherms with the R^2 values of 0.9371 and 0.9966 respectively. The Freundlich isotherm model revealed better suitability. The experimental data were analyzed with RSM modeling using Design-Expert software. ANOVA results with coefficients of determination (R^2 = 0.9643 and adjusted R^2 value = 0.9516) for CAF removal confirmed the existence of a good agreement between the experimental and predicted values. Furthermore, the 3D surface plots of RSM also revealed that all the three operating parameters studied are significant in the removal of CAF. Furthermore, the positive results obtained in this study regarding adsorption demonstrated the suitability of SD for the various types of real wastewaters contaminated with CAF molecules.

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