Removal of 3-chloroaniline from aqueous solution by treated coffee waste: isotherm modelling and thermodynamic studies

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ABSTRACT
3-chloroaniline (3CA) concentrations were measured in aqueous solution by UV/Vis spectrophotometer. Validation of the calibration curve’s linearity, instrumental precision (RSD%), limits of detection and quantification were accomplished. The coefficient of calibration curve (1.0–10.0 mgL\(^{-1}\) 3CA) had a high correlation (R\(^2\) = 0.9997) and the instrumental precision was in the range (RSD% = 0.50–0.74%, n = 10). The LOD and LOQ from the regression analysis were 0.20 mgL\(^{-1}\) and 0.61 mgL\(^{-1}\), respectively. A treated coffee waste adsorbent was utilised for 3-chloroaniline removal by process of sorption from aqueous solution. The major components of the coffee waste are the hemicellulose, cellulose, and lignin. The temperature effect (25°C, 35°C and 45°C) on sorption was evaluated, with sorption decreasing by increasing of temperature which reached 87%, 75% and 54%, respectively. Isotherms type L were found and associated with monolayer sorption. The parameters of sorption were examined by employing Langmuir, Freundlich and Dubinin-Radushkevich sorption models. The isotherm models of Langmuir and Dubinin-Radushkevich had acceptable correlation coefficients (R\(^2\) = 0.87–0.88). The Langmuir and Dubinin-Radushkevich sorption capacities of 3-chloroaniline were found to be 44 to 50 mgg\(^{-1}\). The values of separation factor (R\(_s\)) were ranging from (0–1) which indicated a favourable sorption. In thermodynamic study, the physical sorption process was confirmed by van’t Hoff equation. In addition, the free energy ΔG\(^*\) (−19.1 kJmol\(^{-1}\)) and enthalpy ΔH\(^*\) (−56.6 kJmol\(^{-1}\)) had negative values which suggested that the sorption was spontaneous, and the process was exothermic.

1. Introduction
Chloroaniline is a crucial organic additive commonly applied in medicine, chemical industries, plastics and pesticides. Besides, it is also a widespread pollutant, which has a high degree of persistence, toxicity, accumulation and it is hard to be naturally degraded. The production of effective methods to eliminate the chloroaniline compounds from wastewater and their use as resources is still a major issue [1,2].

In the recent past, researchers conducted some analysis inside potato stores and they noticed that traces of 3-chloroaniline (3CA) compound was found on the air [3–8]. The researchers argued that the presence of 3CA could be because of thermal degradation of chlorpropham (CIPC) that takes place during the fogging process. Chlorpropham (CIPC) is...
a member of the N-Phenyl Carbamate group. The IUPAC name for this compound is isopropyl 3-chlorocarbanilate and the ISO common name is chlorpropham. It is utilised as a potato sprout inhibitor for long-term storage. The molecular structures of CIPC and its main metabolite 3CA are presented in (Figure 1).

Globally, it is estimated that close to 11% of the pesticides in use contain CIPC in their composition and mix. CIPC has a weak bond known as labile bond [9]. The bonds are weak and thus the process of breakdown is relatively fast and easy. Therefore, making the compounds a suitable replacement for the organochlorides. However, scientific studies have cast a shadow of doubt over concerns related to the compound on human health and the environment. It is a known fact that carbamates breakdown into aniline derivatives which are known as environmental pollutants. That notwithstanding, the aniline-based derivatives are known carcinogenic components. Additionally, farmers are in the practice of using CIPC as a sprout suppressant in potatoes.

It is important that stored potatoes are protected from sprouting in order to minimise losses on the farmers. A good sprout inhibitor should help the stored product maintain its quality and not cause harm to the consumers. Carbamic acid esters are thermolabile and sensitive to degradation if stored under undesirable conditions such as in excessive heating. CIPC is one of the carbamate groups that are prone to breakdown into aniline compounds if stored under inappropriate conditions [10]. Thermal fogging temperatures can reach up to (300–600°C) and as the fog containing CIPC comes into contact with the hot aluminium pipes, it degrades at the high temperatures to release 3CA. Additionally, apart from the thermal degradation of the CIPC compounds, it is further established that constant warming and humidity of the stored potatoes encouraged bacterial growth. In return, the microbes are also responsible for microbial degradation of CIPC into 3CA [4,11].

There are still no studies which show the direct carcinogenic effect of 3CA, however, 3CA is especially toxic to renal and haematopoietic systems [12]. 3CA was also suggested to be toxic as it has a similar structure to 4-chloroaniline (4CA) which is considered to be genotoxic and carcinogenic [11,13]. CIPC continues to be used in more than 90% of all existing applications. It will however be lowered because in some countries in particular the European Union, the ban on CIPC has started [6].

![Figure 1. Chlorpropham (CIPC) and 3-chloroaniline (3CA) structure.](image-url)
Many approaches are currently being used to remove chloroaniline compounds from wastewater effluents, for instance photodegradation [14], hydrodehalorination [15], oxidation [16], biodegradation [17], electrochemical oxidation [18] and sorption [19,20]. Amongst all, sorption is a reliable method that has been applied widely because of its effectiveness, simplicity, rapidness, cost effectiveness and the possibility of organic pollutants being recovered as reuse resources. Sorption is considered as an influential wastewater technology for the removal of amine compounds [21]. Several adsorbent materials have been utilised for the removal of amines from industrial effluents such as clay [22], carbon nanotubes [23] and activated carbon [24]. Also, resin [25,26] has many applications to treat and re-utilise waste water especially hyper-crosslinked resin which has a powerful ability for re-generation and high sorption’s capacity [27]. The surface modifications, that can greatly improve the sorption selectivity, can develop custom-designed sorption resins with unique functional groups [1].

David et al. [28] investigated the photochemical and ultrasonic degradation of CIPC and 3CA in aqueous solution. Both methods were effective, but the ultrasonic method was much significant mainly at (482 kHz) in comparison with (20 kHz). In the degradation of CIPC, the principal metabolites identified were, 3CA, carbon dioxide, carbon monoxide, chloride ions and formic acid. The 3CA degradation also leads to CO, CO2, and Cl−.

In semicontinue-activated sludge reactors, a bioaugmentation method incorporating multiple techniques was employed in the degradation of 3 chloroaniline (3CA) by Bathe, Schwarzenbeck and Hausner, 2009 [29] using strain of Comamonas testosterone and a population of mixed bacteria. Simillar study using Comamonas testosterone strain was conducted by (Boon et al. [30,31]) and with Comamonadaceae strain [32]. Hinteregger et al. [33] characterised the ring cleavage of 3CA by Pseudomonas acidovorans. In the study by [34] several isolated bacteria that could, if there’s no other source of nitrogen or carbon, degrade 3CA and 3,4-DCA have been isolated. While the most commonly known genera belong to the β-subclass of Proteobacteria (Pseudomonas, Acidovorax, Acromobacter, Delfia and Comamonas). The authors demonstrated that 3CA and 3,4DCA can be degraded by diverse bacterial species. This in agreement with other studies using Delfia tsuruhatensis strain [35].

Z. Liu et al. [1] studied the sorption of 4CA in aqueous solution using hyper cross linked and estimated the thermodynamic parameters. The efficiency of sorption reached 98%. Also [36], studied the applicability of activated carbon that was prepared from the Para cashew shell after chemical activation with ZnCl2 to remove 4-chloroaniline and 4-bromophenol from wastewater. The authors concluded that the material has a high effectiveness at 45°C with sorption capacity of 552 mgg−1 and 488 mgg−1 for 4-chloroaniline and 4-bromophenol, respectively. A new-found Brevibacillus strain from the finishing and dyeing factory with the toxic 4-chloroaniline (4CA or PCA) was isolated and studied by [37].

Most early studies as well as current literature work have focused mainly on 4CA, while only few works have conducted on 3CA. The preparation of activated carbons from different agricultural wastes or plant biomasses to remove 3CA is still a fruitful area that is opened for research. Therefore, this study aims to prepare activated carbons from coffee wastes and examine its sorption capacity and efficiency to remove 3CA from aqueous solution. This includes several isotherm models and thermodynamic studies.
2. Materials and methods

2.1. Chemicals and adsorbent

3-Chloroaniline (3CA): 99% purity from ACROS ORGANICS (108581000–100 mL) Lot#A0359627. Methanol (purity ≥ 99.9%) was purchased from (Sigma Aldrich, United Kingdom).

Commercial coffee waste was collected from cafeteria and used as adsorbent. Coffee wastes were oven dried at 70°C for 48 h, mixed with concentrated H₂SO₄ at 100°C for 24 h, then neutralised with NaHCO₃ solution and rinsed extensively with deionised water and oven dried at 70°C for 48 h. Eventually, sieved at a uniform size of 300 μm and stored.

2.2. Preparation of 3-chloroaniline solutions

A stock solution of (1000 mgL⁻¹) of 3CA in 100% methanol was prepared. Smaller concentrations were prepared by dilution in deionised water. The solubility of 3CA is very high in methanol and modest in water (6.2 gL⁻¹ at 20°C). It can be prepared directly in 100% water but traces of methanol in the solution help to increase the stability [4].

2.3. Validation of UV-Vis spectrophotometer

The prepared 3CA standards in methanol solvent and aqueous solution were determined by UV/Vis spectrophotometer (Biochrom Ltd, Cambridge, model: 80–7000-21, S.N: 114239). To record the spectra and locate the maximum absorption (λmax), the standardised instrument was scanned from 400 to 200 nm. In addition, linearity of the calibration curve, instrumental precision (RSD% or CV), limits of detection and quantification (LOD, LOQ) were assessed.

2.4. The 3CA sorption onto the coffee waste's activated carbon

2.4.1. Effect of contact time

0.10 g of coffee waste’s adsorbent was put in 100 mL conical flask and mixed with 50 mL of 60.0 mgL⁻¹ 3CA in aqueous solutions. The flasks were placed on the shaker at 130 rpm and incubator (model ZWY100H, CE ISO9001, S.N: 433DDA19) at 25°C, 35°C, 45°C. At every time interval (0, 30, 60, 90, 120, 150, 180,210, 230 min.), an aliquot was filtered by a 0.2 μm a syringe PTFE filter. Samples were determined via UV/Vis spectrophotometer at 236 nm and the sorption% was plotted versus time (min). All experiments were conducted at pH 7.

2.4.2. Sorption isotherm

The equilibrium of sorption isotherm is important to define a substance’s retention from the aqueous media to a solid phase. 3CA sorption isotherm from aqueous solutions were obtained by applying the batch technique. 0.10 g of coffee waste’s adsorbent was put in 100 mL conical flask containing 50 mL of 3CA in aqueous solutions of various concentration levels (C₀) ranges from 0–350 mgL⁻¹ and placed in the shaker and incubator for 4 h. Then solutions were filtered and analysed by a spectrophotometer at 236 nm. Experiment
was repeated three times at three different temperatures (25,35,45°C). The concentration at equilibrium ($C_e$) was obtained.

The adsorbed amount $q_e$ (mg g$^{-1}$) is estimated by Equation 1

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$  \hspace{1cm} (1)

$C_e$ and $C_0$ are the equilibrium and initial concentrations (mg L$^{-1}$) of 3CA in liquid phase, respectively; $m$ (g) the adsorbent mass and $V$ (L) is the solution volume.

2.4.3. **Calculation of isotherms parameter**

A series of models have been used to illustrate equilibrium between adsorbed 3CA at constant temperature from aqueous solution. Model equations and fitting were the main issue for the study of sorption mechanisms. Diversion of the fitted isotherm from the true isotherm was inevitable due to experimental errors. These isotherm models allow the parameters and sorption to be properly represented, and the essence of sorption phenomena to be understood. Three models (Table 1): Langmuir, Freundlich, and Dubin-Radushkevich (DR) were used to facilitate the estimation of 3CA sorption potential for the waste coffee grounds at different temperatures.

2.4.4. **Thermodynamic study**

Sorption parameters at various temperatures have been studied. Van’t Hoff’s Equation was evaluated to consider the feasibility and existence of the sorption by means of Gibbs free energy ($\Delta G^°$), enthalpy ($\Delta H^°$) and entropy ($\Delta S^°$); through the following equations:

$$\Delta G^° = -RT \ln(K)$$  \hspace{1cm} (2)

$$K_a = \frac{\alpha_{AS}}{\alpha_A \times \alpha_S}$$  \hspace{1cm} (3)

$$\ln(K_a) = -\frac{\Delta H^°}{RT} + \frac{\Delta S^°}{R}$$  \hspace{1cm} (10)

The activity equilibrium constants $K_a$, in chemical equilibrium of non-ideal mixtures were calculated from Equation 11:

$$K_a = \frac{\alpha_{AS}}{\alpha_A \times \alpha_S} = \frac{y_{AS}}{y_A \times y_S} \times \frac{m_{AS}}{m_A}$$  \hspace{1cm} (11)

$$a_i = y_i \times m_i$$  \hspace{1cm} (12)

where:

- $\alpha_i$ = activity$_i$
- $y_i$ = activity coefficient$_i$
- $m_i$ = molality$_i$
Table 1. Sorption models.

| Models                  | Equation                                      | Linear Equation                           | Parameters                                                                 |
|-------------------------|-----------------------------------------------|-------------------------------------------|---------------------------------------------------------------------------|
| Langmuir               | $q_e = \frac{q_{\text{max}} bC_e}{1 + bC_e}$ | $\frac{1}{q_e} = \frac{1}{q_{\text{max}} bC_e} + \frac{1}{q_{\text{max}}}$ | **Langmuir equation:** $q_e$ (mgg$^{-1}$): amount of 3CA adsorbed per gram of coffee waste weight at the equilibrium state. $b$: affinity constant for the binding sites $q_{\text{max}}$ (mgg$^{-1}$): The maximum sorption amount onto the surface’s monolayer. |
| Frendlich              | $q_e = K_f C_e^n$                             | $\ln q_e = \ln K_f + n \ln C_e$          | **Frendlich equation:** $n$ and $K_f$ are empirical constants.             |
| Dubinin - Radushkevich| $q_e = q_{\text{max}} e^{(-BErT)^{0.5}}$     | $\ln q_e = \ln q_{\text{max}} - Be^{2}$    | **Dubinin-Radushkevich equation:** $B$: constant of sorption energy. $e = RT \ln (1 + 1/C_e)$; Polanyi potential (Polanyi [49]); $R$: gas constant (8.314 J mol$^{-1}$ K$^{-1}$); $T(K)$: absolute temperature. $E$: mean sorption energy. Characteristic energy for the system. |
in diluted systems and pure solid (ideal-dilute solution), it is usually assumed:

\[ \alpha_S = 1, \text{ because } S \text{ is a pure solid.} \]
\[ \gamma_A = 1, \text{ because the solution is dilute.} \]
\[ \gamma_{AS} = 1, \text{ coefficient of equal activity of sorbate at vacant and adsorbed site of adsorbent (as pure solid), and Equation 13 becomes:} \]
\[ Ka = \frac{m_{AS}}{m_A} \]

which can be expressed as:

\[ Ka = \frac{\text{mol}_A/\text{KgAS}}{\text{mol}_A/\text{KgSol}} = \frac{\text{mg}_A/gS}{\text{mg}_A/gSol} = \frac{\text{mg}_A/gS}{\text{d}(g_{mSol}/mL_{sol}) \times mL_{sol}} \]

and substituting the expressions for \( q_e \) and \( C_e \) in Equation 15. The Equation 16 to calculate \( Ka \) is obtained.

\[ Ka = \frac{q_e(\text{mg}_A/gS)}{C_e(\text{mg}_A/L)} \times 1000(\text{ml/L}) \]

By means of equation 10, \( \Delta S^0 \) and \( \Delta H^0 \) can be determined from the intercept and slope of \( \ln(K) \) versus \( T^{-1} \) plot.

3. Results and discussion

3.1. Coffee waste characterisation

3.1.1. Typical chemical composition

The literature review [38–40] have shown that the major components were the polysaccharides hemicellulose and cellulose. (Table 2) shows the chemical composition of coffee waste. Hemicellulose is a branched heteropolymer, composed of pentose (xylanes), alternating units of mannose and glucose or galactose that differs in composition according to its source. Shorter chain and more branched than cellulose. Cellulose is a linear \( \beta \)-d-glucose connected to glycosidic bond \( \beta \)-(1-4). The molecules of cellulose form rigid structures because of the lack of side chains. Cellulose is more crystalline and water-insoluble relative to hemicellulose [41,42].

In the cell walls of the terrestrial plants Lignin is an alkyl-aromatic polymer. Lignin is a normal, highly effective barrier to microbial attack and allows transport of water and nutrients through plant tissues. Lignin is a structural and rigid system for the plants. The heterogeneity and lack of a fixed primary structure makes lignin unique as a biopolymer.

Minerals elements present in coffee ground are various such as Potassium, Calcium, Magnesium, Phosphorous and others. (Table 3) shows the mineral composition.
3.1.2. Morphology

Morphological structure of coffee grounds using scanning electron microscope (SEM) has been reported [43]; the adsorbent particles have various shapes and sizes. The surface shows to be rough with cavities over the entire surface with distribution 5 to 10 micrometres.

3.1.3. FTIR spectra

As has been previously reported in the literature [38,39], FTIR spectra of coffee waste showed a strong band between 3000–3600 cm\(^{-1}\) associated to vibration modes of (–NH and – OH) functional groups. Two peaks at 2850 and 2920 cm\(^{-1}\) were related to stretching bonds sp\(^3\) C–H (asymmetrical and symmetrical combination) to both caffeine and lipids. A peak at 1750 cm\(^{-1}\) is correlated to carbonyl vibration (stretching C = O) of the substituted ester groups or aliphatic ester in triglycerides. Peaks in 1750 and 2390 cm\(^{-1}\) (H–C = O, stretching) were assigned as being aldehyde groups. Bands shown at 1130, 1040 and 980 cm\(^{-1}\) were designated to C–O–H and C–O vibration of bonds of carbohydrates as hemicellulose and cellulose. FTIR spectrum was characteristic of lignocellulosic substances.

3.1.4. XRD analysis

Crystallinity by XRD analysis has been reported [38,43]. Pattern diffraction of coffee waste indicated crystalline and amorphous regions. Crystalline regions can be related to the presence of crystalline cellulose, which due to its regularity is less accessible chemically, because of the formation of intermolecular hydrogen bonds. Another major component of the coffee waste, hemicellulose showed a more amorphous structure than cellulose, therefore more easily susceptible to chemical attack. Amorphous region can be assigned to hemicellulose.

| Table 2. Typical chemical composition. |
|--------------------------------------|
| Chemical Components | Composition (g 100 g\(^{-1}\) Dry Material) [38] | Standard Deviation |
|----------------------|-----------------------------------------------|-------------------|
| Cellulose            | 13.6                                          | 0.8               |
| Hemi cellulose       | 38.7                                          | 1.3               |
| Lignin               | 25.5                                          | 1.4               |
| Fat                  | 2.5                                           | 0.6               |
| Ashes                | 1.2                                           | 0.3               |
| Protein              | 18.4                                          | 0.7               |
| Nitrogen             | 2.8                                           | 0.4               |
| C/N ratio            | 17.1                                          | 0.5               |

| Table 3. Mineral composition of coffee ground. |
|-----------------------------------------------|
| Mineral Element | Composition (mg Kg\(^{-1}\) Dry Material) [38] | Standard Deviation |
|-----------------|-----------------------------------------------|-------------------|
| Potassium       | 12.44                                         | 0.05              |
| Calcium         | 2.16                                          | 0.03              |
| Magnesium       | 1.93                                          | 0.06              |
| Sulphur         | 1.72                                          | 0.07              |
| Phosphorous     | 1.91                                          | 0.04              |
| Iron            | 45.66                                         | 0.08              |
| Cooper          | 19.74                                         | 0.05              |
| Cobalt          | 14.92                                         | 0.06              |
Adel et al. [44] used x-ray studies to assess the graphitising ability of activated carbons and classified them into two types. Through carbonisation, non-graphitising carbons form a robust cross-link between the arbitrarily oriented primary crystallites that form an immobile rigid mass. The produced charcoals were intense and preserved even during the following heat-treating period with a well-developed microporous structure. For PVDC (polyvinylidene chloride), an instance of non-graphitising carbon, approximately 65.0% carbon was packed in graphite layers with a medium diameter of 16.0 Å. There were strong disorders with the remaining carbon, 55% of which was divided into pairs of 0.37 nm of parallel planes. The distance was approximately 2.5 nm between simple crystallites. Even at temperatures above 3000°C, the PVDC charcoal was not graphitised. The development of non-graphitising structural elements with robust crosslinks was supported by the presence of oxygen in the original raw material or by a lack of hydrogen.

An example of graphitising carbon is PVC (polyvinyl chloride), where the fundamental crystallites had a soft linkage since the initiation of carbonisation. The charcoal obtained was ineffective, and its porous structure was less developed, however the crystallites had many layers, parallel to each other. The formation of crystallites continued, perhaps by adding layers or even groups of layers, after the removal of non-organised carbon. The difference in graphitising ability seems to be as a result of the variation in crystallite orientation of the two carbon types. The crystalline configuration of activated carbon affects its reactivity considerably. There was a slightly lower chemical reactivity at the basal levels than at edges or at defect areas. Graphited carbons with an identical basal-plane surface were therefore less responsive than amorphous carbons. The oxidation rates at the edge sites of the activated carbon were 17–20 fold higher than at the basal plane’s surface. In the same way, intercalation reactions requiring dimensional shifts in the framework of carbon were only feasible with strongly graphited carbons due to the high-level of order.

The surface of activated carbon also has a chemical’s structure in addition to the crystalline and porous structure. The capacity of sorption of active carbons is dependent on their porous structures or physical interaction, but the chemical structure is highly effective. The dispersive element of the van der walls forces is the crucial component of the sorption on a well-ordered surface. For graphite with complex crystalline and a highly ordered surface, the sorption is mainly defined by the portion of dispersion attributable to London forces. However, while in activated carbon, the disruptive basic micro-crystalline structure causes variations in the arrangement of clouds of electrons in the carbon skeleton. This is maybe because of the existence of deficient or partly burnt graphite layers in the crystallites, which result in the production of unsparing electrons and insufficient saturation of valences and this can affect the sorption.

Almost invariable concentrations of oxygen and hydrogen are correlated with active carbons. They can also be related to halogens, nitrogen, sulphur, and other atoms. Such heteroatoms originate from starting material and through incomplete carbonisation can be a part of the structure or chemically associated with the surface when activated or subsequently treated. Carbon may also adsorb some molecular groups, for example phenols, nitrobenzene, amines, and numerous cationic substances.

Experimental investigations using X-ray diffraction have revealed that molecular species or heteroatoms are linked with the aromatic sheet edges or to defective atomic carbon atoms and cause carbon-sulphur, carbon-oxygen, carbon-hydrogen, carbon-halogen
surface compound or surface complexes. They are also referred to as surface complexes and surface groups. These heteroatoms can also be integrated into the systems of heterocyclic ring in the carbon layers. Since these edges are the principal for surface sorption, they alter surface properties and characteristics by the existence of those molecular species or surface compounds [45]. Groups of carbon-oxygen on the surface have also influenced the sorption of the inorganic and organic compounds from solutions. Al-Deqs et al. [46] and Goyal et al. [47] investigated the sorption of various anionic and cationic dyes on specific carbon blacks and charcoals and found that the sorption was highly affected by the occurrence of acidic oxides surfaces besides the carbon surface area. Carbon oxidation increases with the expansion of oxygen on the surface, and the sorption of cationic dyes increased and decreased with the removal of these surface oxides during evacuation. Regarding on the anionic dyes, oxidation decreased sorption, based on the change in acidic groups quantity. Goyal and his co-workers [47] have researched the impact on many active carbons with specific surfaces and related to varying levels of carbon oxygen surface groups on the sorption of many metal ions, for instance Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Cr$^{3+}$, and Cr$^{6+}$(VI). The researchers found that the sorption could not be associated with the surface alone, but rather relied on the oxygen and acid-oxygen groups on the surface. The sorption of those ions reduced through degassing and improved on oxidation. When oxidation increases, sorption would be assigned to the development of surface acidic groups that are ionised in aqueous solution to yield H$^+$ ions to the liquid phase, leave behind the carbon surface negatively charged, allowing the sorption of metal cations to occur. When degassing eliminates these negative sites, the surface of the carbon misses its affinity to adsorb cations.

### 3.2. Validation of UV-Vis spectrophotometer

The UV-Vis spectrophotometer was calibrated, and the performance of the UV-Vis was examined via the verification inspections to make sure that the entire parameters were operating (for example, baseline flatness, accuracy of photometric and wavelength). 3CA standards and blanks were determined. Although 3CA has high water solubility, its stability in methanol is much higher and for this reason the 3CA was formulated in 100% methanol. The spectra of 3CA absorbance versus wavelength is presented in (Figure 2).

The 3CA calibration curve ($R^2 = 0.9997$) at 236 nm is shown in (Figure 3). The spectrum reveals that the first peak was near the methanol cut-off (205 nm) and the cut-off of water (190 nm). The solvent’s cut-off is the wavelength where almost all the incident radiation begins to be absorbed by the solvent. For wavelengths shorter than the cut-off, any absorption data obtained for the analyte will be regarded indistinguishable from noise and considered as a systematic error. Thus, for 3CA determination, the second peak (at 236 nm) was chosen. Furthermore, it is quite essential to maintain the range of absorption in the calibration curve within (0.1–1.0). For this reason, concentrations out the lower (1.0–10.0 mgL$^{-1}$, n = 10) were omitted to acquire accuracy in the results. Any concentration higher than that has been diluted with the identical composition.

The precision RSD% at various concentrations (1.0–10.0 mgL$^{-1}$, n = 10) is shown in (Figure 4) which ranged from (0.50–0.74%). However, at lower concentrations the variation between measurements was higher and less precise in comparison with measurement at higher concentration.
The LOD (0.02 mgL\(^{-1}\)) and LOQ (0.07 mgL\(^{-1}\)) based on ten repetitive measurements (n = 10) of a single concentration of 1 mgL\(^{-1}\) 3CA was determined by equation 17 and 18 in (Table 4).

In addition, they can also be calculated from the 3CA calibration curve using the regression statistics and equations 19 and 20 in (Table 4). The regression analysis is shown in (Table 5).

Hence, the LOD and LOQ based on the calibration curve was found to be (0.20 mgL\(^{-1}\)) and (0.61 mgL\(^{-1}\)), respectively. However, it is advisable to stick to the concentration covered on the calibration curve considering the possible deviations from Beer’s Law.

### 3.3. 3CA sorption on the activated carbon prepared from coffee waste

#### 3.3.1. Effect of contact time

The sorption of 3CA on the surface of treated coffee waste’s activated carbon is shown in (Figure 5). At initial time, the sorption process was fast then becoming slower at a level...
Figure 3. Calibration curve (1.0–10.0 mgL⁻¹ 3CA, n = 10, at 236.0 nm) in aqueous solution.

Figure 4. Averaged precision for absorbance of (1.0–10.0 mgL⁻¹ 3CA, n = 10, at 236.0 nm) in aqueous solution.

Table 4. LOD and LOQ equations based on a single and multiple concentrations.

| Method | Equation | Equation No. |
|--------|----------|--------------|
| Based on a Single Concentration | $\text{LOD (mg/L)} = \left( \frac{\text{LOD Response}}{\text{Mean}} \right) \times 1.0$ | (17) |
| | $\text{LOD Response} = 3 \times \text{STDEV}$ | |
| | $\text{LOQ (mg/L)} = \left( \frac{\text{LOQ Response}}{\text{Mean}} \right) \times 1.0$ | (18) |
| | $\text{LOQ Response} = 10 \times \text{STDEV}$ | |
| Based on the Calibration Curve | $\text{LOD (mg/L)} = \left( \frac{\text{SE of } y \text{-intercept}}{\text{Slope}} \right) \times 3.3$ | (19) |
| | $\text{LOQ (mg/L)} = \left( \frac{\text{SE of } y \text{-intercept}}{\text{Slope}} \right) \times 10$ | (20) |
close to the curve plateau which is a general pattern of a heterogeneous surface. The pattern indicated that with quick sorption at the initial time and a slower rate close to the curve plateau, the process of sorption is heterogeneous. The sorption% for 3CA at (25–45°C) reached 87%, 75% and 54%, respectively. The equilibrium time was 150 min.

### 3.3.2. Sorption isotherms
(Figure 6) indicates the sorption isotherms of 3CA at various temperatures. The form of isotherm observed was L shape, which was concave to the axis of concentration, and has a specified plateau. Type L isotherm is correlated with solute monolayer sorption and has a limited solvent competition. It is apparent that an increase in temperature reduced the sorption potential of the coffee waste.

The linear models associated to the Langmuir, Freundlich and DR are represented in (Figures 7, 8 and 9). According to the correlation’s coefficients (see Table 6) obtained from the trend curves, it seems that the Langmuir and Dubinin–Radushkevich isotherms described the type of sorption. The (Table 6) summarises the parameters values of the theoretical sorption isotherms.

### Table 5. The calibration curve’s regression.

|                | Coefficients   | Standard Error | t-Stat  | P-value | Lower, 95%  | Upper, 95%  |
|----------------|----------------|----------------|---------|---------|-------------|-------------|
| Intercept      | 0.043894737    | 0.004652869    | 9.433908| 0.0025241| 0.02908723  | 0.058702242 |
| X Variable 1   | 0.074304511    | 0.000717953    | 103.49492| 1.989E-06| 0.07201966  | 0.076589359 |

Figure 5. Time impact on 3CA sorption.

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**Figure 5.** Time impact on 3CA sorption.
Figure 6. Sorption isotherms of 3CA on coffee waste.

Figure 7. Linear Langmuir isotherms.

Figure 8. Linear Freundlich isotherms.
Figure 9. Linear Dubinin-Radushkevich isotherms.

Table 6. Parameters of Langmuir, Freundlich and DR models.

| Temp. (°C) | Langmuir | Freundlich | Dubinin-Radushkevich |
|-----------|----------|------------|----------------------|
|           | $q_{\text{max}}$ (mgg$^{-1}$) | b (Lmg$^{-1}$) | $R_L$ | $R^2$ | $K_f$ | $n$ | $\beta$ | $a_{\text{max}}$ (mgg$^{-1}$) | $B$ (mol$^2$J$^{-2}$) | $E$ (KJmol$^{-1}$) | $R^2$ |
| 25        | 45.77    | 0.1370     | 0.129 | 0.871 | 18.45 | 0.175 | 0.843 | 50.96 | 4.97 x 10$^{-9}$ | 10.0 | 0.882 |
| 35        | 44.80    | 0.0608     | 0.247 | 0.849 | 12.46 | 0.233 | 0.806 | 49.48 | 6.93 x 10$^{-9}$ | 8.5 | 0.847 |
| 45        | 44.13    | 0.0259     | 0.427 | 0.867 | 7.05  | 0.311 | 0.778 | 46.26 | 9.77 x 10$^{-9}$ | 7.2 | 0.836 |

For the Langmuir model, sorption takes place without contact between the adsorbed species on a homogenous energy surface through the formation of monolayers. Enhanced interaction between adsorbate and adsorbent occurs in molecular micropores [48].

Polanyi [49] proposed the potential principle of physical sorption for the Dubinin-Radushkevich model. It determines the thermodynamically equivalently sorption potential (sorption energy) of a material from the bulk of liquid to its adsorbed state as the free energy of change (negative value) [50]. In this theory, the adsorbed amount $q_e$ of a particular adsorbate in an equilibrium condition was calculated by the sorption potential and by the isothermal physisorption data that can be expressed in the form of temperature with an invariant curve and energy characteristic.

Assuming the Langmuir isotherm applies, a dimensionless constant named separation factor $R_L$ is defined as the essential characteristic of the Langmuir isotherm by:

$$R_L = \frac{1}{1 + bC_0}$$

(21)

$b$ is the constant of Langmuir and $C_0$ is the initial concentration. The coefficient is employed to determine the viability of sorption, it means that the isotherm is favourable when $0 < R_L < 1$, irreversible when $R_L = 0$, unfavourable when $R_L > 1$ and linear when $R_L = 1$. The $R_L$ values for different temperatures were determined in (Table 6). $R_L$ values ranged from 0–1, showing clearly that the sorption was favourable.

To evaluate the sorption differences at different temperatures, an ANOVA analysis was carried out from $q_e$ at $C_0 = 60$ (mgL$^{-1}$), with respect to the sorption temperature. Results are shown in (Table 7).
The analysis of variance (p-value < 0.05) validates the influence of temperature on the sorption capacity of coffee waste.

In the literature review, 3CA sorption experiments in aqueous solutions on different adsorbents have been investigated, with different characteristics including materials such as: kaolinite [51], potato peel [4] and exchange resins [52]. (Table 8) summarises the 3CA sorption capacities of these materials. The sorption isotherms reported have shown a typical behaviour as the one observed in (Figure 6), with formation of the plateau after saturation of sorption centres.

Angioi et al. [51] evaluated two adsorbents Na-montmorillonite (SWy-1) and clays kaolinite (KGa-1) to adsorb selected chloroanilines at concentration levels between 1.0 and 10.0 mgL$^{-1}$. They showed that montmorillonite had more sorption potential in comparison to kaolinite; 3CA sorption coefficients were 0.0030 Lg$^{-1}$ for kaolinite and 0.0105 Lg$^{-1}$ for montmorillonite, the researchers suggested that the difference was due to structures of adsorbents.

Zr and Al hydroxy-intercalated bentonite (HAIMX80, HZrMX80) and Zr, Al-pillared bentonite (Zr-MX80, Al-MX80) were evaluated by Matthes and Kahr [53] as adsorbents of 3CA. Isotherm were described with Freundlich model, HAI and HZrMX80 exhibit medium-affinity sites ($K_F$ 0.16 and 0.12), and A1 and ZrMX80 high-affinity sites ($K_F$ 3.5 and 1.6). Reported sorption s are showed in (Table 8). The authors point out that sorption was related to the basicity of anilines and the acidity of the sorbent.

Szczepanik et al. [54] measured the sorption of 3CA on activated and non-activated halloysye, applied Langmuir equation to report capacities values and describing a multicentre sorption. The active centres number that takes part in the process of sorption were not whole numbers, for 3CA was 1.26. Therefore, they propose

Table 7. Analysis of variance.

| Temperature (°C) | n  | Mean | St.Dev | 95% Confidence Interval |
|-----------------|----|------|--------|-------------------------|
| 25              | 3  | 25.58| 0.13   | (24.54–26.63)            |
| 35              | 3  | 21.98| 0.84   | (20.94–23.03)            |
| 45              | 3  | 16.96| 0.68   | (15.91–18.00)            |

Source DF Adj. MS F – value p-value

| Temperature | 2  | 56.3368 | 102.47 | 2.30 x 10$^{-5}$ |
| Error       | 6  | 0.5498  |        |               |
| Total       | 8  |         |        |               |

Table 8. Sorption capacities of 3CA on adsorbents.

| Adsorbent | Sorption Capacity (mg g$^{-1}$) | Reference |
|-----------|---------------------------------|-----------|
| Kaolinite (KGa-1) | 0.03 | (Angioi et al. [51]) |
| Na-montmorillonite (SWy-1) | 0.105 | (Angioi et al. [51]) |
| Al-Hydroxy intercalated bentonite HAIMX80 | 0.40 | (Matthes & Kahr [53]) |
| Zr-Hydroxy intercalated bentonite HZrMX80 | 0.69 | (Matthes & Kahr [53]) |
| Al – pillared bentonite AIMX80 | 1.14 | (Matthes & Kahr [53]) |
| Zr – pillared bentonite ZrMX80 | 1.17 | (Matthes & Kahr [53]) |
| Acid activated halloysite H25/80 | 2.14 | (Szczepanik et al. [54]) |
| Non-activated halloysite HC | 1.84 | (Szczepanik et al. [54]) |
| Co(ll) loaded carboxylated diaminoethyl sporopollenin (ligand exchange resin.) | 327.9 | (Uçan & Ayar [52]) |
| Coffee waste | 45.77 | This study |
a mechanism with different centres on the complex aluminosilicate structure of the halloysites.

Only the ligand exchange resin has a reported value of capacity higher than coffee waste indicating a great affinity onto Co(II) matrix. In a comparative study of chloroanilines sorption, Mustafa and Ayar [52] suggested that sorption capacity was steady with the contribution of secondary balance effects in the sorption, since the sorption of 3CA may not be satisfactorily exemplified by the Langmuir isotherm. It was probably taking place due to coordination of amine to the outer metal Co$^{2+}$ and concluded that a combination of steric hindrance and electrical forces were engaged in sorption.

3.3.3. Thermodynamic parameters

The temperature effect on the sorption of 3CA by coffee waste is illustrated in (Figure 10). The adsorbed amount of 3CA declined to some extent with rising temperatures.

To understand the process of sorption, thermodynamic parameters such as changes in standard entropy ($\Delta S^o$), standard enthalpy ($\Delta H^o$), and standard free energy ($\Delta G^o$), were evaluated. The values of $\Delta H^o$ and $\Delta S^o$ could be acquired from intercept and the slope value, respectively, of the straight line of the plot (Figure 11) of van’t Hoff equation, $\ln (K)$ against $T^{-1}$. The thermodynamic parameters are summarised in (Table 9).

The negative value of $\Delta G^o$ ($-19.1$ kJ mol$^{-1}$) indicates that the 3CA sorption process on the coffee waste is spontaneous. The $\Delta H^o$ value ($-56.6$ KJ mol$^{-1}$) implies that the sorption is an exothermic process. The negative $\Delta S^o$ ($-125.8$ J K$^{-1}$ mol$^{-1}$) decreasing the random order in the interface of solid-solution as 3CA is adsorbed.

The activation energy values (10.0, 8.5 and 7.2 kJ mol$^{-1}$) obtained by the DR model for sorption is typical of physical sorption. Usually, higher activation energies (40–800 kJ mol$^{-1}$) suggest chemisorption, while the physical sorption has energies in the range of (5–40 kJ mol$^{-1}$).

Due to the chemical composition of the coffee waste probably the sorption of 3CA occurs by several mechanisms with different sorption centres. The pKa of 3CA (3.521) [55] indicates that at pH 7 the dissociated fraction is very small (1 ionic:10,000 no ionic), so the neutral specie is predominantly adsorbed and the low activation energy values, suggest physical sorption by weak electrostatic forces, polarisation, electric dipole moments (van

![Figure 10](image.png)

**Figure 10.** Temperature effect on the sorption capacity of 3CA by coffee waste.
der Waals), and π-stacking interactions [1]. The value of ΔH° (−56.6 KJ mol\(^{-1}\)) is near to hydrogen bonding range (8–50 KJ mol\(^{-1}\)). Therefore, during the sorption process hydrogen bond may also play a major role.

D-R isotherms hypothesised that the occupation of micropores is not preceded by formation of multilayers, but sorption occurs by mechanism of instantaneous volumetric filling, so the capacity of sorption is determinate by volume of micropore [56]. The correlation with this model suggests micro-pore filling.

4. Conclusion

In aqueous solution, 3-chloroaniline (3CA) concentrations were evaluated by UV/Vis spectrophotometer. Validation of linearity of the calibration curve, instrumental precision (RSD% or CV), limits of detection and quantification (LOD and LOQ) were accomplished. The standard calibration curve had a high correlation coefficient \(R^2 = 0.9997\) for range \((1.0–10.0 \text{ mgL}^{-1} \text{ 3CA})\) and the instrumental precision was in the range (RSD % = 0.50–0.74%, \(n = 10\)). The LOD and LOQ from the regression analysis were 0.20 mgL\(^{-1}\) and 0.61 mgL\(^{-1}\), respectively.

A treated coffee waste’s adsorbent was utilised for 3CA removal from water by sorption. The major components of the coffee waste are the hemicellulose, cellulose, and lignin. The temperature (25°C-45°C) on sorption was evaluated, with sorption decreasing

\[
y = 6.8018x - 15.128
R^2 = 0.994
\]

Figure 11. \(\ln(K)\) vs \(T^{-1}\).

| \(\Delta G^\circ\) (kJmol\(^{-1}\)) | \(\Delta H^\circ\) (kJmol\(^{-1}\)) | \(\Delta S^\circ\) (JK\(^{-1}\)mol\(^{-1}\)) |
|-----------------|-----------------|-----------------|
| −19.1           | −56.6           | −125.8          |

Table 9. Thermodynamic parameters.
by increasing of temperature. Isotherms type L were found and associated with monolayer sorption. The parameters of sorption were examined by applying several sorption isotherms such as Langmuir, Freundlich and Dubinin-Radushkevich. The Langmuir and Dubinin-Radushkevich isotherm models have acceptable correlation coefficients ($R^2$). The Langmuir and Dubinin-Radushkevich sorption capacities of 3CA were found to be 44 to 50 mg g$^{-1}$. The values of $R_L$ were (0–1) which indicated a favourable sorption.

ANOVA analysis on the sorption capacities corroborated influence of temperature. Sorption capacities that have been reported in literature were lower than those found for coffee waste in this study, except for ligand exchange resin whose capacity was the highest. The physical sorption process was confirmed by van’t Hoff equation. The standard free energy ($\Delta G^\circ$) and enthalpy ($\Delta H^\circ$) had negative values which indicated that the sorption was spontaneous, and the process was exothermic. The sorption of 3CA could occurs by several mechanisms with different sorption centres.

Since the adsorbent used in this study is abundant and available, it is considered a potential adsorbent material for 3CA removal from aqueous fluids and suitable for the wastewater treatment.

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Author contribution
The author (Bandar R. M. Alsehli) planned and designed the experiments; conducted the tests; analyzed the data; provided reagents, materials and methods for analysis and wrote the article.

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