

Equilibrium, Kinetics and Thermodynamic Study of 2-Chlorophenol Adsorption from Simulated Wastewater onto Bone Char

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ABSTRACT

Numerous agricultural wastes, like cow bones, are underutilized in Nigeria, causing significant environmental solid waste menace. Incidentally, large amount of wastewater containing high concentrations of toxic organic compounds such as 2-chlorophenol (2-CP) are continuously being generated due to increased industrial and agricultural activities. Waste cow bones when suitably treated could serve as a good adsorbent for efficient removal of 2-CP from wastewater and also serve as a means of recycling bone wastes from various slaughterhouses in Nigeria. In this study, bone char labeled BC500-120 was produced by carbonization of treated waste cow bones at 500°C for 120 minutes. Characterization of the BC500-120 was carried out using BET surface area analysis, FTIR and SEM/EDX spectroscopy. Sorption experiment was conducted on the effect of constant time, solution pH, initial concentration of 2-CP and constant temperature on the adsorption of 2-CP onto BC500-120 from simulated wastewater. The Langmuir isotherm, Freundlich isotherm and kinetic models: (pseudo first order model, pseudo second order model and the Elovich model) were used to analyze the experimental data. The thermodynamic parameters were estimated from the Langmuir's Constant. Adsorption capacity and removal efficiency of 151.70 and 98.3 % were attained and equilibrium was found to occur between 40-45 minutes. Adsorption capacity and removal efficiency were also observed to be maximum at an initial concentration of 0.09mol/L and pH=7.0 and better favored at higher temperatures. The removal of 2-CP was described by the Langmuir isotherm and the pseudo second order model, and calculated to be 557.05gmin⁻¹mol⁻¹ with an initial rate of 0.00072molg⁻¹min⁻¹ and equilibrium capacity of 0.00114mol/g. The adsorption process was found to be physical, spontaneous and endothermic. The results of the study indicated that BC500-120 can be used as an effective adsorbent for 2-CP removal from liquid wastes.

Keywords: Equilibrium, Kinetics, Thermodynamics, Bone char, 2-chlorophenol.

INTRODUCTION

Most industrial effluents contain chlorophenols which are used by these industries in their daily operations (Prashanthakumar *et al*, 2018). Chlorophenols are derivatives of phenol (Bae *et al*, 2002). They are used as disinfectants, herbicides, insecticides, pesticides, wood preservatives, resins and plasticizers (Fiege *et al*, 2000; Huong *et al*, 2016). Chlorophenols enter the ecosystem via landfill leachate, agricultural run-offs and effluents from industries such as refineries, petrochemicals, pharmaceuticals, polymers, pulp bleaching, chemicals, dyes, textiles and fertilizers (Shen *et al*, 2021). Specifically, 2-chlorophenol (2-CP) is carcinogenic, mutagenic, xenobiotic, highly toxic even at low concentrations (Wang *et al*, 2018; Zada *et al*, 2021). Inhalation of 2-CP causes restlessness, fatigue, gastrointestinal problems, headache, and skin irritation. Acute exposure to 2-CP results in high respiratory rate, shortness of breath, vomiting and nausea (Adane *et al*, 2015). In 1976, the EPA introduced 2-CP as a priority organic pollutant that is hardly biodegradable thus requiring removal from the

aquatic environment as concentrations should not exceed 200µg/L in drinking water (Rezaei *et al*, 2017). Many known methods such as oxidation-reduction, flocculation, chemically induced precipitation, floatation, electrodialysis, reverse osmosis, ion exchange and adsorption have been used successfully to remove 2-CP from wastewater (Kusmierek *et al*, 2021). Amongst these methods, adsorption has emerged the best and most widely used in treating industrial and agricultural wastewater due to its low cost and high efficiency. (Ademiluyi and Nze, 2016; Zaharaddeen *et al*, 2019; Liu *et al*, 2021). Bone waste deposit constitute solid waste menace in the environment. In 2018, Organization for Economic Cooperation and Development (OECD) predicts an increase of 40 million tons of bone waste within the next decade (Alkurdi *et al*, 2019). The use of these bones serves as a means of recycling waste cow bones in various slaughterhouses (Tang, 2019). Bone char has several active sites that can interact with molecules via hydrogen bonding, van der Waals forces, and other chemical attractions (Hart *et al*, 2023). Bone char has been used to remove organic pollutants and heavy metals from wastewater (Reynel-Avila, 2016). The equilibrium, kinetics and thermodynamics of 2-chlorophenol removal from aqueous solution onto bone char has limited research work. This research investigates 2-CP adsorption equilibrium, kinetics and thermodynamics from aqueous solution onto bone char and how time, concentration, pH and temperature affect the removal process. (Tran, 2017) established that the thermodynamic parameters calculated based on the distribution coefficient and the Freundlich constant do not bring physical meanings and therefore should be avoided in calculating the thermodynamic parameters. This research also aims to estimate the thermodynamic parameters from the Langmuir's constant (Zang *et al*, 2011; Ghosal *et al*, 2015; Barakan *et al* 2020; Qu *et al*, 2021).

MATERIALS AND METHOD

Sample Collection and Preparation

Waste cow bones were obtained from Big Government Slaughterhouse in Ikpoba Hill, Benin City, Nigeria (GPS coordinates: 6°9' 52.02" N 5°37'22.22" E). The bones were thoroughly washed with hot water in order to clean up and remove the fat present in the bone cavities. The bones were pre-heated at 150°C for 2 hours to melt up the congealed fat. It was mechanically reduced to smaller sizes, re-washed and oven-dried. The small-sized bone samples were carbonized in an oxygen-free environment at a temperature of 500°C for 2 hours using carbolite AAF 1100 MUFFLE FURNACE and it was allowed to cool in a desiccator at room temperature. The charred sample was crushed with mortar and pestle and then sieved with an Endecott sieve (145µm) and the particles with larger surface area were collected for the experiment.

Preparation of Simulated Wastewater

Stock solution of 2-chlorophenol was prepared by adding 10ml of 9.64mol/L 2-CP into a 100ml volumetric flask and was made to the mark with distilled water and the solution was then labeled 0.964mol/L 2-CP. Standard solutions of 2-CP (0.09mol/L, 0.08mol/L, 0.07mol/L, 0.06mol/L, 0.05mol/L, 0.04mol/L, 0.02mol/L) were prepared by measuring out 9.34ml, 8.30ml, 7.26ml, 6.22ml, 5.20ml, 4.15ml, and 2.07ml of 0.964mol/L respectively into 100ml volumetric flask and made to the mark with distilled water.

Determination of Initial pH of BC500-120

The initial pH of BC500-120 was obtained by weighing 3g into a beaker followed by the addition of 10ml distilled water. The mixture was allowed to stand for 30minutes. After 30 minutes, it was determined by the use of JENWAY 3020 pH meter.

Characterization of BC500-120

Scanning Electron Microscopy (SEM) Micrograph and Energy Dispersive X-ray (EDX) Analysis

The surface morphology of BC500-120 was obtained using Scanning Electron Microscopy (**Hitachi SU 3500 scanning microscope, Tokyo, Japan**) working at a high voltage of 30kV. BC500-120 was coated with gold nanoparticles for conductivity and high-quality SEM images. Afterwards, the coated sample BC500-120 was placed on the sample holder for analysis.

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

To determine the functional groups contained in the carbonized sample BC500-120, FTIR analysis was performed. Prior to analysis, sample tablets were made by combining each sample with KBr (1:100). The samples were then placed inside the FTIR chamber. With an FT-IR spectrometer (Infrared spectrometer Varian 660 MidIR Dual MCT/DTGS Bundle with ATR) equipped with a detector at 4 cm⁻¹ resolutions and 200 scans per sample, the spectra were recorded in the frequency range of 4000 cm⁻¹ to 500 cm⁻¹.

Batch Adsorption Experiments and Process Variables

Varying Initial Concentration

A conical flask was filled with 0.5g of bone char BC500-120 and 10ml of the working concentrations of 2-chlorophenol (0.09mol/L, 0.08mol/L, 0.07mol/L, 0.06mol/L, and 0.05mol/L). The mixture was stirred for 40 minutes using a magnetic stirrer before being filtered through Whatman No. 1 filter paper. A UV/Vis Spectrophotometer was used to determine the residual 2-chlorophenol concentration in the filtrate. Next, the amount adsorbed was calculated using the following equation (Hart *et al*, 2023):

$$q_e = \left(\frac{C_o - C_e}{m} \right) V \quad (1)$$

Where

q_e = Amount adsorbed at equilibrium in (mol/g),

C_o = Initial concentration of 2-chlorophenol in (mol/L),

C_e = Equilibrium concentration of 2-chlorophenol in (mol/L),

V = Volume of 2-chlorophenol used in L,

M = Mass of bone char BC500-120 in grams (g).

The removal efficiency at any given point were determined using the equations below (Wang *et al*, 2020)

$$RE = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (2)$$

Varying Solution pH

10ml of 0.06mol/L 2-chlorophenol and 0.5g of BC500-120 were combined in a beaker to test the impact of solution pH. The solution pH was initially discovered to be 8.8, and it was changed to the appropriate pH levels by adding a few drops of either 0.5M HNO₃ or 0.5M NaOH. After 40 minutes, the reactor was shut off, the content was filtered, and a UV/Vis Spectrophotometer was used to determine the amount of 2-chlorophenol that remained in the filtrate.

Varying Solution Temperature

10ml of 0.06M 2-CP and 0.5g of BC500-120 were weighed into a beaker, and the mixture was stirred with a magnetic stirrer for 40 minutes at 15^oC (a temperature that was attained using an ice bath). The mixture was then filtered through Whatman No. 1 filter paper. A UV/Vis Spectrophotometer was used to determine the residual 2-chlorophenol concentration in the filtrate. A repetition of this process was conducted at 25^oC, 35^oC, and 45^oC, respectively.

Adsorption Isotherms

The equilibrium data obtained were fitted into the Langmuir and Freundlich models to observe the behavior of 2-CP on the surface of BC500-120. At equilibrium a relationship exists between the concentration of the

species in solution and the concentration of the same species in the adsorbed state, that is the number of species adsorbed per unit mass of the adsorbent (Tran *et al*, 2020). Mahmoud *et al* (2012) reported that the linearized form of the Langmuir isotherm can be mathematically represented as:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (3)$$

Where

q_e = Adsorption capacity at equilibrium (mg/g)

C_e = Equilibrium concentration of solute (mg/L)

Q_m = Maximum monolayer adsorption capacity (mg/g)

b = Langmuir isotherm constant (dm^3/mg)

While the linearized form of the Freundlich isotherm is given by:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where

q_e = Adsorption capacity at equilibrium (mg/g)

C_e = Equilibrium concentration of solute (mg/L)

K_f = Freundlich isotherm constant (mg/g)

n = Adsorption intensity

Adsorption Kinetics

To compute the rate at which 2-CP was being adsorbed from the simulated wastewater, the pseudo first and second order model and the Elovich model were applied to the kinetic data. The adsorption of 2-CP onto BC500-120 was modeled using linear and non-linear kinetics analysis and the R^2 values were used to decide the goodness of fit (Musah *et al*, 2022). The linearized and integrated form of the pseudo first and second order model according to Ebelegi *et al*, 2020; Ademiuyi and Nze, 2016, is given by:

For pseudo first order model,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

where k_1 (1/min) is the pseudo-first-order rate constant, q_e (mg/g) is the adsorption capacity of the adsorbent at equilibrium, q_t (mg/g) is the adsorption capacity at time t .

For pseudo second order model,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (6)$$

If the initial rate of adsorption is $k_2 (q_e)^2$ ($\text{mol g}^{-1} \text{min}^{-1}$), the plot of (t/q_t) against t from the equation above gives a linear relationship whose slope and intercept can be used to determine q_e and k_2 respectively (Edet and Ifebugu, 2020).

According to Edet and Ifelebuegu, (2020), the Elovich equation is given as:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (7)$$

Where

α is the initial adsorption rate (mol/g/min), β is the desorption constant (g/mol).

Assuming $\alpha\beta t \gg 1$ and applying boundary conditions, the equation becomes; (Farouq and Yousef, 2015)

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (8)$$

If the process fits the equation, then a plot of q_t against $\ln(t)$ would give a linear relationship with the slope of $1/\beta$ and an intercept $(1/\beta) \ln(\alpha\beta)$.

Adsorption Thermodynamics [Hameed and Foo (2010); Gueu *et al.*, 2007; Soto *et al.*, 2011]

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated by combining the equations given by Charles (2006) and Zawani *et al.*, (2009):

$$\Delta G^\circ = RT \ln K_L \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

Combining equation (9) and (10) gives equation (11):

$$\ln K_L = \frac{-\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (11)$$

Where

K_L = Standard thermodynamic equilibrium constant L/g ($\frac{q_e}{C_e}$) (Tran *et al.*, 2016)

q_e = Adsorption capacity at equilibrium (mol/g)

C_e = Equilibrium concentration of solute (mol/L)

T = Absolute temperature (K)

R = gas constant (8.314 J/mol.K)

RESULTS AND DISCUSSION

Characterization of BC500-120

The specific surface area of inactivated BC500-120 as determined by BET analysis was 50.54 m²/g, which is comparable to Tang *et al.*, (2019) published value of 59.62 m²/g.

Scanning Electron Microscopy (SEM) Micrograph and Energy Dispersive X-ray (EDX) of BC500-120

The micrograph in Fig.1 revealed the surface morphology of BC500-120 obtained from thermal treatment. The image revealed that BC500-120 was characterized by homogeneous surface. Visual introspection revealed a hexagonal shape, porosity, regular surface topography with little roughness and fracture. EDX analysis of

elemental composition of BC500-120 confirms the presence of carbon, oxygen and silicon as major constituents along with traces of phosphorus, aluminum, potassium, and calcium.

Sample ID: SEM/EDX micrograph sample 01 BG1 160820231033

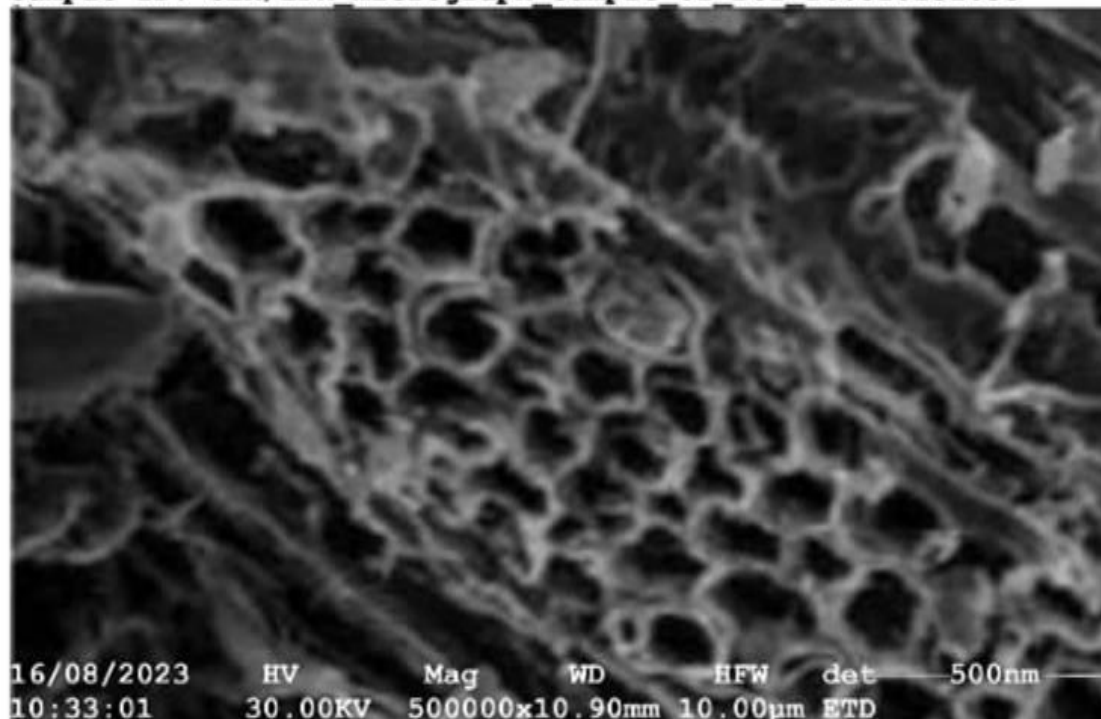


Fig. 1. SEM image (BC500-120)

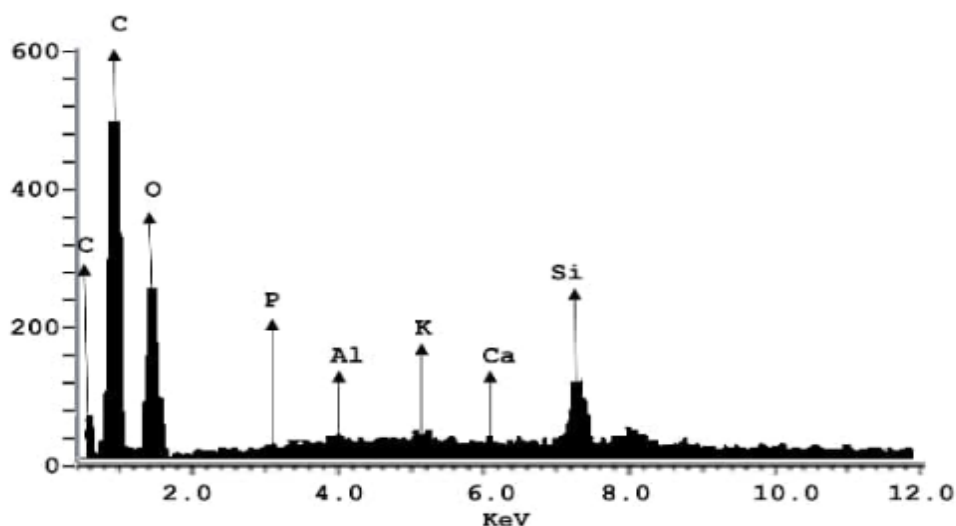


Fig. 2. EDX Analysis (BC500-120)

Fourier Transform Infrared Spectroscopy (FTIR) Spectrum of BC500-120

The FTIR spectrum of BC500-120 is shown in Fig. 3. The sharp and weak signal observed at 3708.25cm^{-1} may be due to -OH stretching vibration of the phenolic groups of lignin or the hydroxyl group of hydroxyapatite. Also, the sharp and medium signal observed at 2710.01cm^{-1} may be due to -CH stretching vibrations of the aromatic rings while the medium and sharp signal observed at 2600.10cm^{-1} may be due to C=O stretching vibrations of residual collagen or calcium carbonate. In the fingerprint region, the peaks at 1240.55cm^{-1} , 1108.36cm^{-1} , 998.15cm^{-1} , and 863cm^{-1} may be due to the asymmetric stretching vibration of CO_3^{2-} group, the silicon-oxygen bond vibration, phosphorus-oxygen vibration of the PO_4^{2-} group and symmetric stretching vibration of the CO_3^{2-} group.

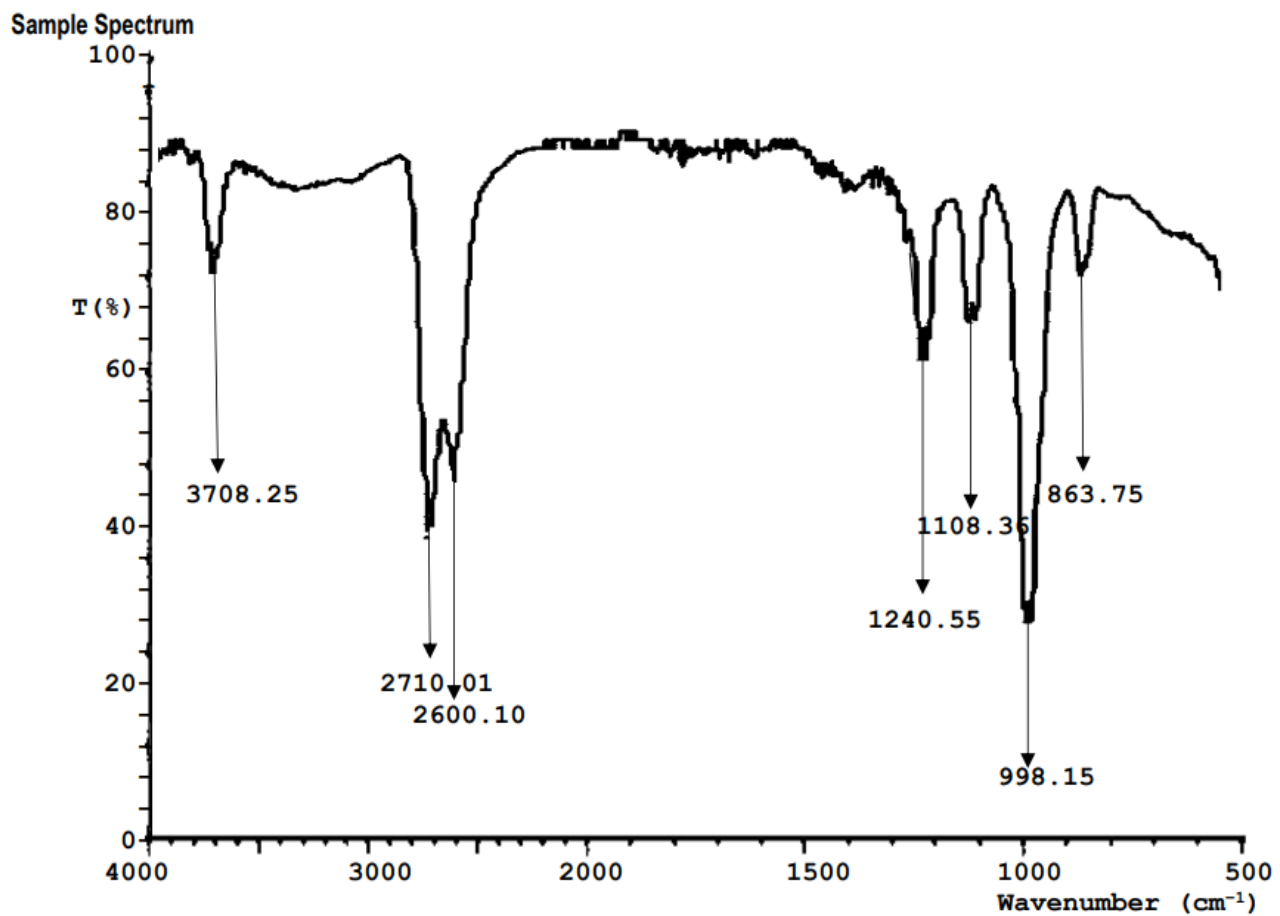


Fig. 3. FTIR Spectrum (BC500-120)

Effect of Process Variables on the Removal Process of 2-CP

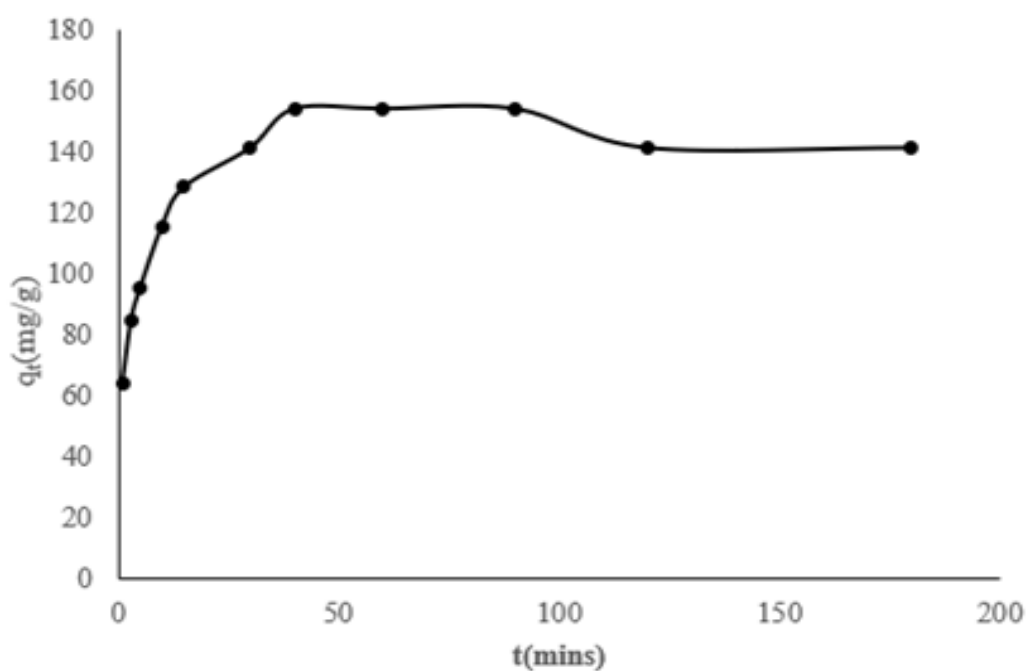


Fig. 4. Effect of contact time on capacity adsorption

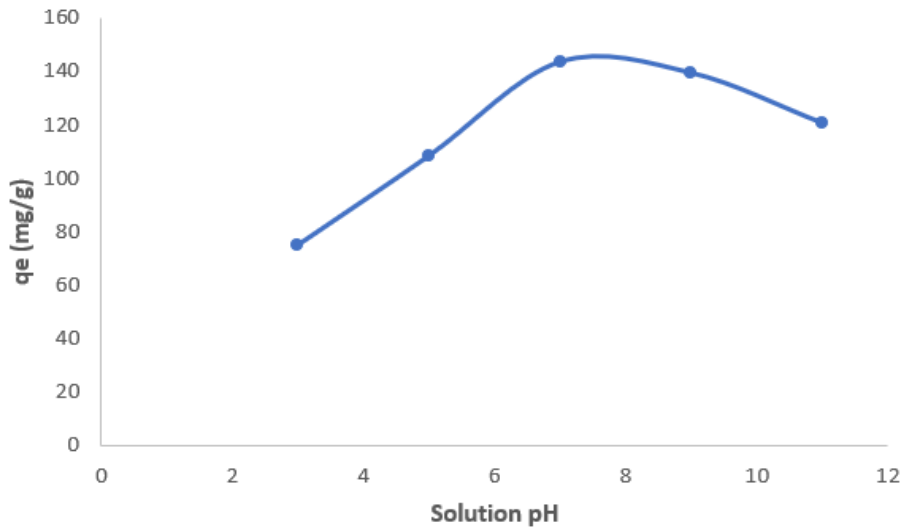


Fig. 5. Effect of solution pH on capacity adsorption

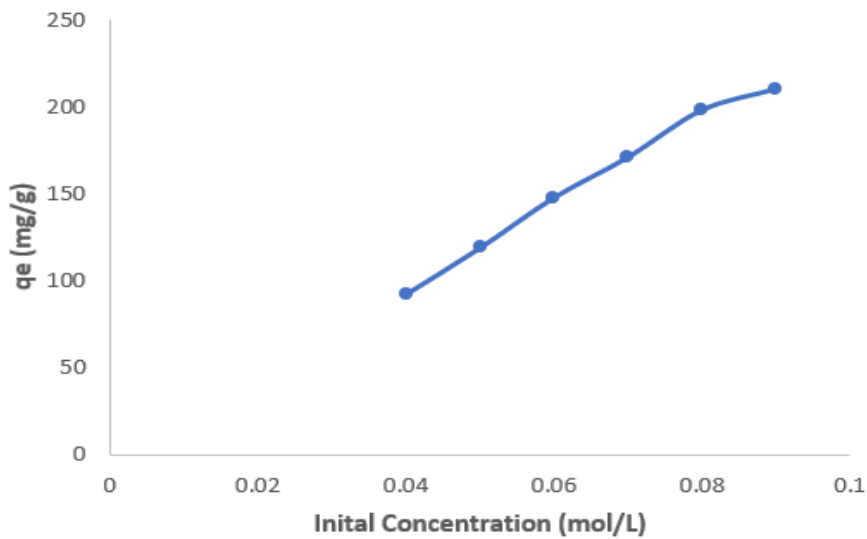


Fig. 6. Effect of Initial Concentration on capacity adsorption

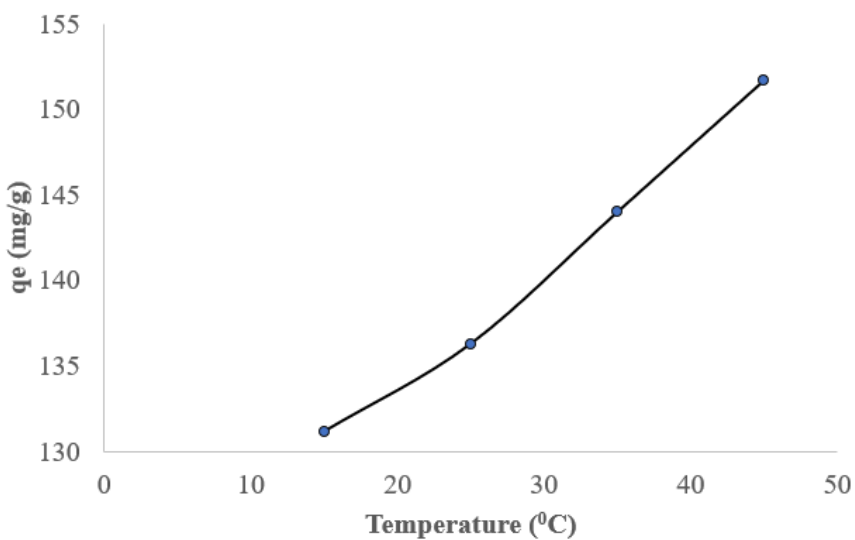


Fig.7. Effect of solution temperature on capacity

Effect of Contact time

As is obvious from Fig. 4, an increase in the contact time allows more time for the 2-CP molecules to interact with the adsorption sites of the bone char BC500-120 resulting in increased adsorption capacity. It was observed that the adsorption process hit equilibrium at about 40 minutes with q_e of 0.0012mol/g (154.27 mg/g). Afterwards, no significant increase in adsorption capacity was recorded.

Effect of Solution pH

The adsorption capacity of BC500-120 is impacted by changes in solution pH, which also affects the surface charge of BC500-120 and the ionization behavior of 2-CP. Fig. 5 showed that the adsorption capacity increased from 74.82 to 143.47 when the pH was adjusted from 3 to 7. Moving on, the capacity adsorption was observed to decrease gradually. Thus, 7 was determined to be the ideal pH for 2-CP adsorption. This could be because of the net negative charge on the effective surface of bone char BC500-120 and the electrostatic repulsion between the 2-chlorophenolate ion formed in an acidic medium. In basic medium, the same behavior was also noted. Capacity adsorption was found to be 143.47 at a neutral pH of solution; this could be because of the intermolecular hydrogen bonding between 2-CP and the lignin component of BC500-120. Jiang *et al*, (2016) noted comparable outcomes.

Effect of Initial Concentration

Fig. 6 showed that when the concentration of 2-CP increased from 0.04 to 0.09 mol/L, the adsorption capacity increased from 92.5 to 210.07mol/g. The uptake of 2-CP molecules is made possible by available active sites at high dilutions leading to a higher capacity adsorption. Since the same number of active sites of 0.5g BC500-120 remain the same compared to the increase number of 2-CP molecules leading to a decrease in adsorption capacity at lower dilutions, any decline in adsorption capacity later observed with increased initial concentration may be due to saturation of active sites of BC500-120 after equilibrium has been established. It is deduced from capacity adsorption data that concentrations less than 0.09 are the effective removal limits for 2-CP. This 2-CP trend is comparable to Wang *et al*, (2020) findings.

Effect of Temperature

From Fig. 7, it was observed that capacity adsorption of 2-CP increases from 72.71 to 151.03mol/g with a corresponding increase in temperature from 15 to 45°C indicating that the adsorption of 2-CP was initially favored at higher temperatures. This may be due to various reasons such as dilution of pore size of BC500-120, increased number of active sites or the decrease in the thickness of the boundary layer surrounding BC500-120 resulting in the reduction of resistance to mass transfer. Also, a decrease in % removal was observed at temperatures 35 to 45°C and this may be due to a rapid increase in the kinetic energy of 2-CP and desorption of 2-CP from the surface of BC500-120.

Table 1. Isotherm parameters for the adsorption of 2-CP onto BC500-120

| <i>Isotherm</i> | <i>Parameters</i> | <i>Value</i> |
|-------------------|--|--------------|
| <i>Langmuir</i> | q_{\max} (mg/g) | 212.76 |
| | K_L (L/mg) | 0.0027 |
| | R_L | 0.9998 |
| | R^2 | 0.9963 |
| <i>Freundlich</i> | K_F (mg ^{-1-1/n} L ^{1/n} g ⁻¹) | 26.728 |
| | N | 1.3380 |
| | R^2 | 0.1740 |
| | $1/n$ | 0.7474 |

Table 1 showed the values of both the Freundlich and Langmuir isotherm constants and their respective correlation coefficients. By comparison, the Langmuir isotherm best fit the equilibrium data with R^2 value of 0.9963 which is highly and more correlated than that obtained by fitting the equilibrium data into the Freundlich model.

RESULTS OF KINETIC STUDIES

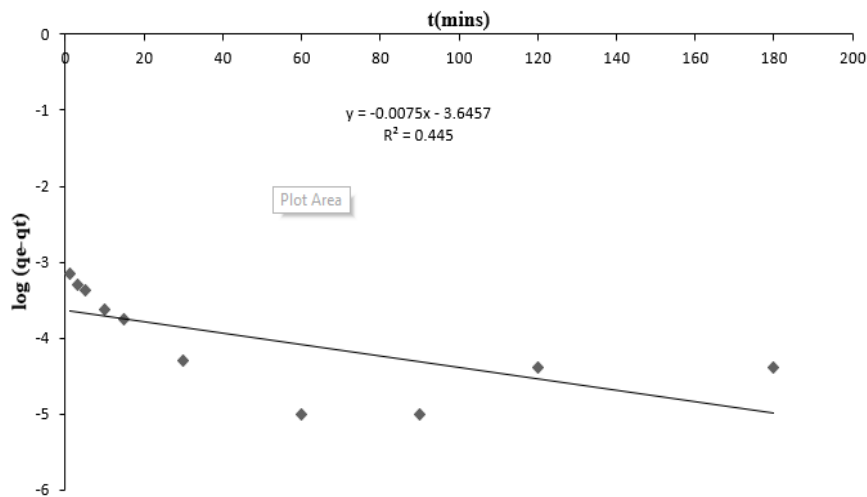


Fig. 8. Pseudo first order model

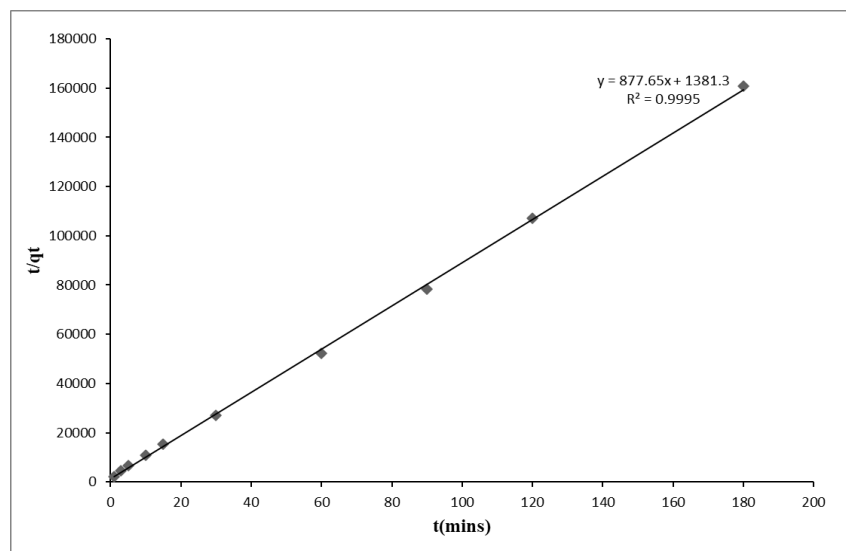


Fig. 9. Pseudo second order model

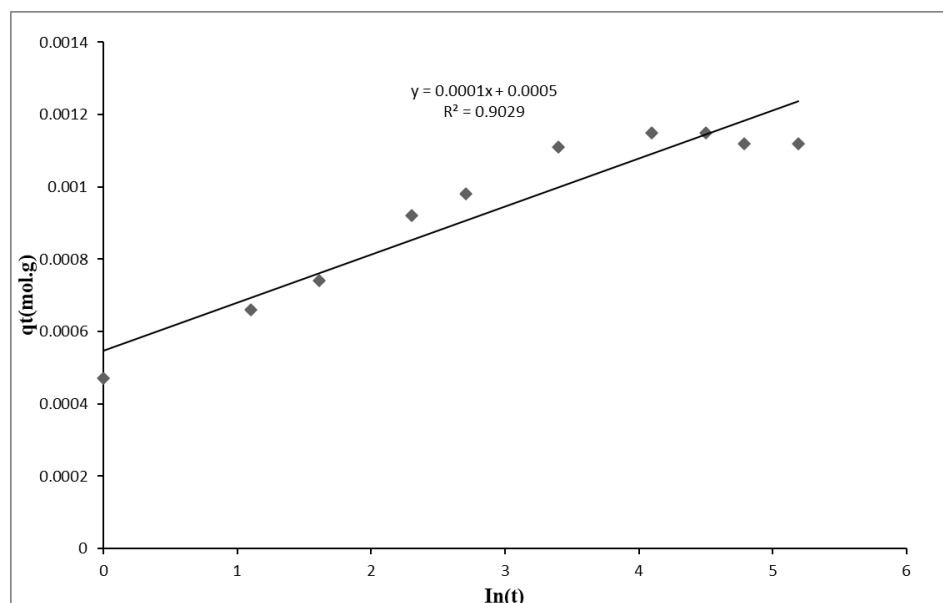


Fig. 10. Elovich model

Table 2. The Outcome of Kinetic parameters

| | R^2 | q_e (mol/g) | k_1 (min^{-1}) | k_2 (g/min/mol) | h ($\text{molg}^{-1}\text{min}^{-1}$) | α (mol/g/min) | β (g/mol) |
|---------------------------|--------|---------------|-----------------------------|-------------------|---|----------------------|-----------------|
| Pseudo first order model | 0.445 | 0.00023 | 0.0173 | | | | |
| Pseudo second order model | 0.9995 | 0.00114 | | 557.05 | 0.00072 | | |
| Elovich model | 0.903 | | | | | 1.6045 | 7692.31 |

The results of kinetic models were determined from the slope and intercept of the work plot. K_1 and q_e which are equilibrium rate constant and adsorption capacity of bone char BC500-120 were found to be 0.0173min^{-1} and 0.00023molg^{-1} respectively, with an R^2 value of 0.445. K_2 and q_e for the pseudo second order model were also observed to be $5571.05\text{gmin}^{-1}\text{mol}^{-1}$ and 0.00114molg^{-1} respectively, with an R^2 value of 0.995. The initial rate of adsorption h ($k_2q_e^2$) was $0.00072\text{molg}^{-1}\text{min}^{-1}$. α and β which are the initial adsorption rate and desorption constant for the Elovich model were observed to be $1.6045\text{molg}^{-1}\text{min}^{-1}$ and 7692.31gmin^{-1} , with an R^2 value of 0.903. On the strength of a higher correlation coefficient and a q_{ecal} value of 0.00114mol/g within the range of the experimentally determined q_e of 0.00116mol/g , the outcome of kinetic analysis therefore indicated that the adsorption of 2-CP onto bone char was best fitted and is best described by the pseudo second order model.

Table 3. Thermodynamic parameters estimated from the Langmuir's Constant

| Temperature | | $1/T$ | K_L (q_e/C_e) | $\ln K_L$ | R (J/kmol) | ΔG^0 (KJ/mol) | ΔH^0 (KJ/mol) | ΔS^0 (J/kmol) |
|--------------------|-----|-----------|---------------------|-----------|--------------|-----------------------|-----------------------|-----------------------|
| $^{\circ}\text{C}$ | K | | | | | | | |
| 15 | 288 | 3.472E-03 | 0.11 | -2.21 | 8.314 | 5.29 | 58.73 | 183.27 |
| 25 | 298 | 3.356E-03 | 0.15 | -1.90 | 8.314 | 4.71 | 58.73 | 183.27 |
| 35 | 308 | 3.247E-03 | 0.28 | -1.27 | 8.314 | 3.25 | 58.73 | 183.27 |
| 45 | 318 | 3.145E-03 | 1.18 | 0.17 | 8.314 | -0.45 | 58.73 | 183.27 |

The thermodynamic experiments were conducted at four different temperatures viz: 15, 25, 35 and 45°C . The ΔH^0 and the ΔS^0 values were calculated from the slope and intercept of the work plot. From Table 3, the values of (ΔG^0) were found to decrease with increasing temperature and the conclusion on adsorption mechanism was drawn based on the magnitude of the standard enthalpy change ΔH^0 and not based on the standard Gibb's energy change ΔG^0 (Luo *et al*, 2015). For chemisorption the magnitude of ΔH^0 is $>80\text{kJ/mol}$ while for physisorption it is less than 40kJ/mol (Thue *et al*, 2020; Chang *et al*, 2014; Lipkowski *et al*, 2002).

CONCLUSION

The result of this study showed that BC500-120 is a very good adsorbent for removing 2-CP from aqueous media. The results obtained from sorption experiment revealed optimum pH of 7.0-7.3, optimum concentration of 0.09mol/L , optimum time of 40 minutes, contact temperature of 45°C and removal efficiency of 98.3%. The removal of 2-CP was described by the Langmuir isotherm and the pseudo second order model. The rate of 2-CP removal was calculated to be $557.05\text{gmin}^{-1}\text{mol}^{-1}$ with an initial rate of $0.00072\text{molg}^{-1}\text{min}^{-1}$, rate constant of $5.571 \times 10^2\text{gmin}^{-1}\text{mol}^{-1}$ and equilibrium capacity of 0.00114mol/g . The outcome of thermodynamic analysis revealed that the adsorption process was physical, spontaneous and endothermic.

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