Equilibrium, Thermodynamics, Kinetics of Adsorption of CO_3^{2-} and SO_4^{2-} Ions on Modified Plantain Peels

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Received: 04 October 2023/ Revised: 16 October 2023/ Accepted: 21 October 2023/ Published: 31-10-2023

Abstract**—** *To reuse treated wastewater, water quality must be improved. Adsorption is a simple, cost-effective method for eliminating toxicities and poisnous anions. The adsorbent's features and properties determine the method's effectiveness. This research examines the adsorption of carbonate and sulphate anions onto plantain peels modified with 2-amino-4,6-dihydridoxypyrimidine. Characterization was done using SEM, XRD, and FTIR. UV-visible spectroscopy was used to measure initial and equilibrium concentrations, and Langmuir and Fremdliuch isotherms were used to analyze the data. The best parameters for adsorbing 150 mg/L* CO_3^{2-} *and* SO_4^{2-} *were: pH 2, and 4, 0.8 g adsorbent, 120 min contact time, and 330 K temperature. Kinetic study used pseudo-first-order reaction equations, and both ion uptake processes followed pseudo-first-order rate expression.* ΔG *(-3.772 kJ/mol) for* CO_3^{2-} *and* ΔG *(-3.047 kJ/mol) for* SO_4^{2-} *were negative, and* ΔH *(-22.04 kJ/mol) and (-39.92 kJ/mol) were also negative, indicating the adsorption process was feasible, spontaneous, and exothermic. Modified plantain peels had high adsorptivity and were a cost-effective adsorbent for* CO_3^{2-} *and* SO_4^{2-} *from aqueous solutions.*

Keywords**— 2-amino-4,6-dihydridoxypyrimidine, Anions, Isotherm, Plantain peels, Thermodynamic.**

I. INTRODUCTION

Toxic anions polluting groundwater is a global problem endangering drinking water. Excessive use and discharge of phosphorus, nitrogen, and sulphur compounds raise nutrient levels in surface and groundwater. When toxic metals enter the environment, metal ions accumulate in humans through direct ingestion or food chains. Water is a fundamental resource for humanity, and its protection is essential for present and future societies. Human activities, like industrial practices, domestic waters, and agricultural uses (e.g. fertilizers, compost, wastewater treatment effluent) often contaminate water with nitrate, sulphate, and phosphate[1]. Recent technological and economic developments are creating toxic pollutants in the different sources of natural water and this is constituting a major hazard to human health [3]. With over 1.2 billion people lacking access to clean, unpolluted, and safe drinking water, water-related issues especially as regards the ever-increasing water scarcity and water pollution remains one of the most topical issues of environmental [2]. Higher levels of sulfate in drinking water lead to its bitter taste and digestive problems as well as corrosion of sewer pipes in addition to causing problems in the anaerobic wastewater treatment processes [4].

Improving water quality is essential for wastewater reuse. Health risks must be taken into account, which could lead to stricter water quality standards [5]. Common mercury removal techniques include adsorption [6], ion exchange, flocculation, and ultrafiltration. Adsorption is a simple, adaptable, and established technique for removing heavy metals, including mercury, from industrial wastewater [7]. It is cost-effective and does not require advanced technology. Deep filtration, macro-filtration, and adsorption can remove some toxic anions, while disinfection eliminates the rest [7].

Wastewater purification using adsorption is a simple, economical way to remove toxins and metals. The adsorbent's features and properties determine the method's effectiveness. Adsorption isotherm is the fundamental concept in adsorption. Equilibrium between pressure/concentration in the bulk fluid phase and adsorbed quantity is known as adsorption. Banana peel and its modified forms are cost-effective and widely available, making them popular adsorbents for wastewater treatment (5-

6). Cellulosic agricultural waste, such as banana peel, is abundant, cheap, and can remove heavy metals from wastewater. It has been demonstrated to have a high capacity for heavy metal removal[9].

Several studies have explored the adsorption of heavy metals onto solid surfaces for separation and pre-concentration of complex mixtures, single elements, and series [10]. Reverse osmosis and filtration are expensive for developing countries like Nigeria, so low-cost adsorbent materials are needed to remove anions and heavy metals globally [11].

Thus, this research is, therefore, an inclusive part of the ongoing process of developing an alternative technology for utilizing cheap plantain peels modified with 2-amino 4,6-dihydroxylpyrimidine (ligand) to study the kinetics, equilibrium, and thermodynamics of adsorption of carbonate (CO_3^{2-}) and sulphate (SO_4^{2-}) anion on modified plantain peels.

II. MATERIALS AND METHODS

2-amino-4,6-dihydroxylpyrimidine (ligand) was obtained from Sigma Aldrich, India. All other reagents were of analytical grade. Plantain peels were bought from a local market in Ajah, Lagos Island, Nigeria. Deionized water was used throughout.

2.1 Preparation of Modified Biosorbent

1.5 g of the ligand was dissolved in 1000ml sodium hydroxide and stirred until colorless. Samples of 5 g, 10 g, and 25 g were weighed and mixed with 50ml, 70ml, and 100ml of ligand respectively. The mixtures were shaken for 70 hours to ensure the ligand was well adsorbed by the plantain peels. The reaction process is as follows:

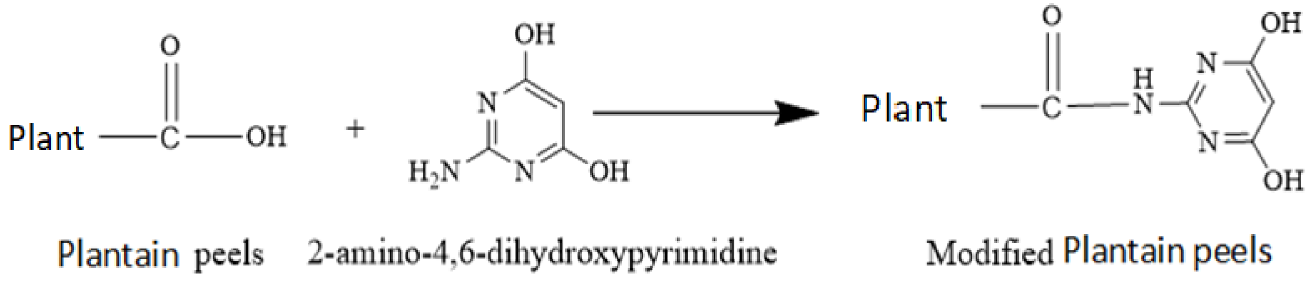

FIGURE 1: Reaction between plantain peel and the ligand

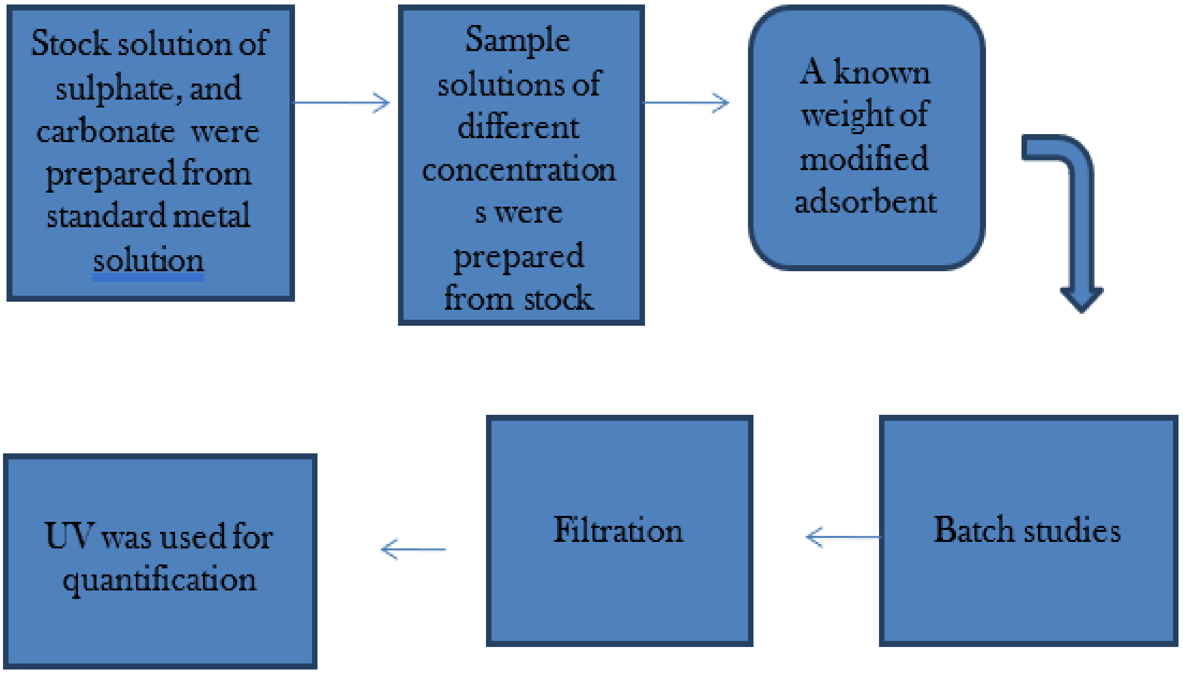

FIGURE 2: Organogram for sample preparation and quantification

FIGURE 3: (a, b, c, and d): Dried plantain peels, pulverized plantain peel, modified plantain peel on shaker, and dried modified plantain peel respectively.

2.2 Adsorption Kinetics

Adsorption kinetics offers insights into the adsorbent's service time, adsorption mechanisms, and adsorption-adsorbent interactions. However, choosing appropriate models for sorption data analysis is challenging due to the plethora of kinetic models. The adsorption kinetic was studied at 25 ^{0}C using 0.2 g in 100 mL solution at 100 mg/L, sampled at intervals until 150 min. UV-Vis spectrophotometry at 800 nm and 420 nm determined the final carbonate and sulphate concentrations. Equation (1) calculated the adsorption capacity.

$$q_t = \frac{Ci - Cf}{m} \times V \tag{1}$$

Where q_t is the adsorption capacity at time t, C_i and C_f are the initial and equilibrium concentration respectively, in mg/ L, V is the volume of the solution and m is the mass of the adsorbent in g

The kinetics of adsorption can be described by different models, some of which include:

Pseudo-first order Lagrange model considers the rate of change that occurs in the uptake of adsorbate at a particular reaction time to be directly proportional to the difference in the concentration and rate at which the adsorbate is removed with time. The model is represented by the equation below:

$$\frac{dqt}{dt} = K_t\ (q_e - q_t) \tag{2}$$

The integral form is given as;

$$\text{Log } (q_e\text{-}q_t) = \text{Log } (q_e) - (\frac{K_t}{2.303})t \tag{3}$$

Where $\mathbf{q_e}$ (mg/g) is the adsorption capacity of the adsorbent at equilibrium.

$\mathbf{Q_t}$ (mg/g) is the adsorption capacity of the adsorbent at time, **t**.

$\mathbf{K_t}$ (per min) is the rate constant for pseudo-first-order adsorption.

The plot of Log ($\mathbf{q_e}$-$\mathbf{q_t}$) versus **t** gives a relationship that is linear from which $\mathbf{K_t}$ and $\mathbf{q_e}$ can be determined from the slope and intercept of the plot.

Pseudo-second-order kinetics: The pseudo-second-order model proposes that the rate of adsorption is proportional to the square of the concentration of the adsorbate on the surface. This model takes into account the possibility of a two-step adsorption process, involving chemisorption or strong physical adsorption [13]. It provides a better fit for adsorption processes where the initial concentration is closer to the equilibrium concentration. The model assumes that one metal ion is adsorbed onto two sorption sites on the adsorbate surface. The PSEUDO-SECOND ORDER linear expression is given as:

$$\frac{t}{q} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t \tag{4}$$

2.3 Adsorption Isotherm

Freundlich and Langmuir models are two of the most popular adsorption isotherm models for activated carbon in water and wastewater treatment [14]. They describe the relationship between adsorbate concentration and adsorbent loading. This research studied adsorption isotherm models. Adsorption is a process where adsorbate and adsorbent come into contact and equilibrium isotherm is established when the adsorbate concentration in the solution is balanced with the interface concentration [15]. The Langmuir isotherm, for monomolecular adsorption, is:

$$q_e = \frac{q_m K_L C_e}{1+K_L} \tag{5}$$

The linearized form of the equation is given as:

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{6}$$

Where **C$_e$** is the equilibrium metal concentration, **K$_L$** and **q$_m$** are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (1/mg) respectively.

The Freundlich Isotherm Model is another approach that is used for the description of the multilayer and heterogeneous adsorption of molecules to the adsorbent surface. This model is demonstrated by the equation:

$$\mathrm{Ln}q_e = \mathrm{Ln}K_f + \frac{1}{n} LnC_e \tag{7}$$

Where **q$_m$** (mg/g) represents the amount of adsorbed molecules to the adsorbent surface at any time, **C$_e$** (mg/L) is the equilibrium concentration, **K$_f$** (mg/g) indicates the adsorption capacity of the adsorbent towards the adsorbate and **n** is an indicator for the degree of homogeneity and describes the distribution of the adsorbed molecules on the adsorbent surface. A value of **n** higher than 1, indicates a favorable adsorption of the molecules onto the adsorbent surface. A value of higher **n** reflects the higher intensity of adsorption.

2.4 Thermodynamic studies

Thermodynamic parameters are very important for adsorption studies, indicating the spontaneity of the adsorption process[17]. The negative value of Gibb's free energy change (ΔG°) for a given temperature indicates the spontaneity of the adsorption process[18]. Among the parameters, Gibb's free energy change (ΔG°) was calculated using Equation (8):

$$\Delta G° = -RT \ln K_a \tag{8}$$

While the change in enthalpy (ΔH°) and change in entropy (ΔS°) were determined using the Equation,

$$\ln K_a = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{9}$$

Where **R** is the gas constant (8.314 J/mol K), **T** is the temperature in Kelvin (K) and, **K$_a$** is the Langmuir constant.

III. RESULTS AND DISCUSSIONS

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

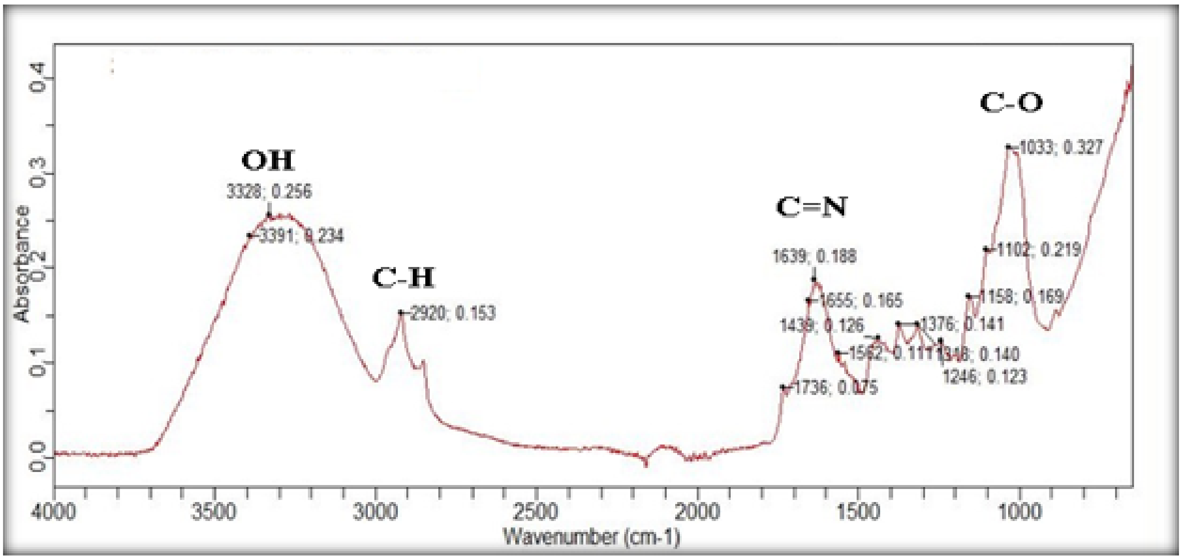

FIGURE 4: FTIR image for modified plantain peel.

FTIR spectrum of modified plantain peel was recorded to identify functional groups coordinating with ions. Figure 4 shows the FTIR spectrum of 1.30 mm size mesh dried plantain peels. The broad band at 3328 cm^{-1} indicates O-H stretching of carboxylic acid. The 2920 cm^{-1} band indicates C-H stretching of alkane, 1639 cm^{-1} is C=N imine stretching, and 1033 cm^{-1} is C-O stretching of primary alcohol. The 1639 cm^{-1} peak confirms ligand presence, indicating modification of plantain peels.

3.2 Scanning Electron Microscope (SEM)

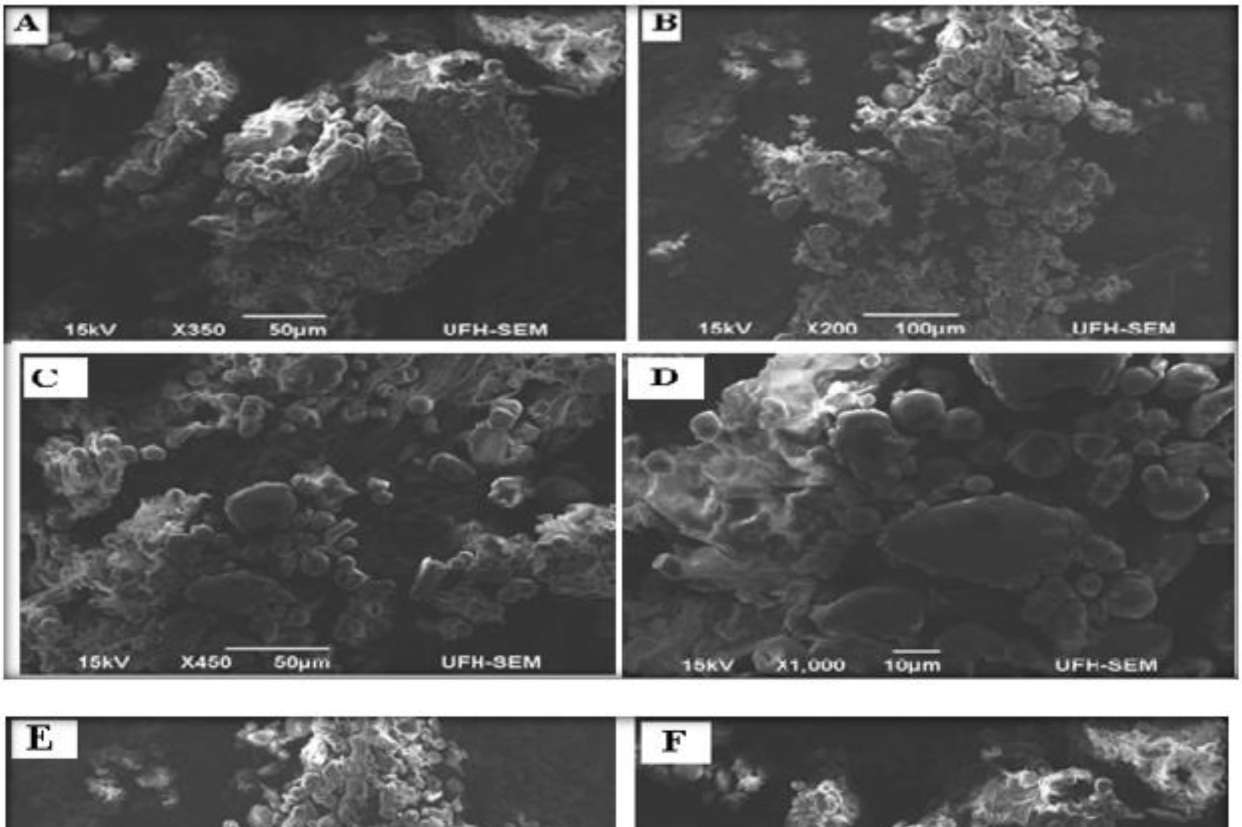

FIGURE 5: (A-D and E-H): SEM images of sieved and unsieved plantain peels before adsorption (A-D and E-H, respectively)

The Scanning electron microscope (SEM) was used to analyze the adsorbate's surface morphology before and after adsorption. Figure 5 displays the results with a different scale bar. SEM also showed the toxic anions adsorbed onto the modified plantain peels. The results showed the adsorbent material's surface morphology, which affects adsorption capacity and efficiency due to features like pore size, cracks, and roughness.

3.3 X-ray Diffraction (XRD)

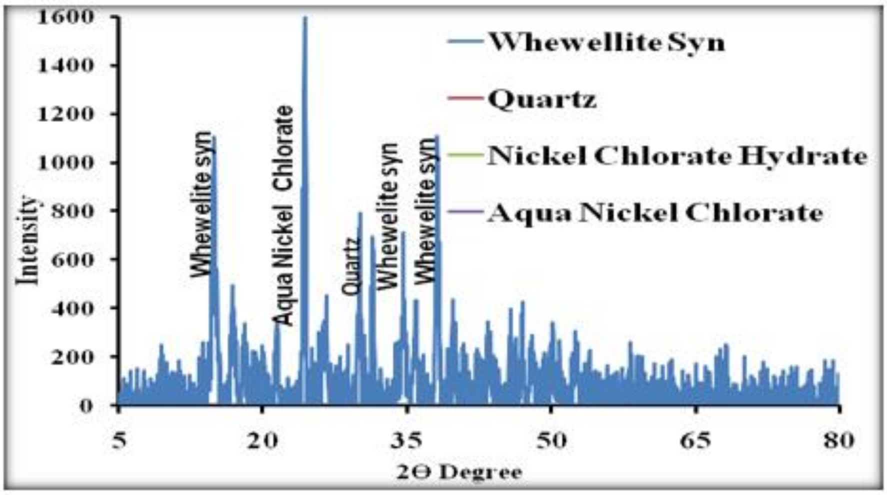

FIGURE 6: XRD image For Pulverized Sieved Plantain Peels

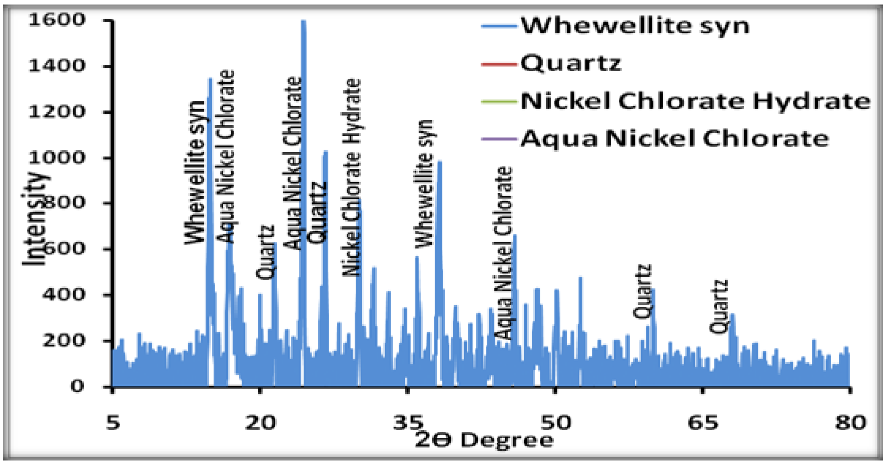

FIGURE 7: Shows XRD For Pulverized Unsieved Plantain Peels

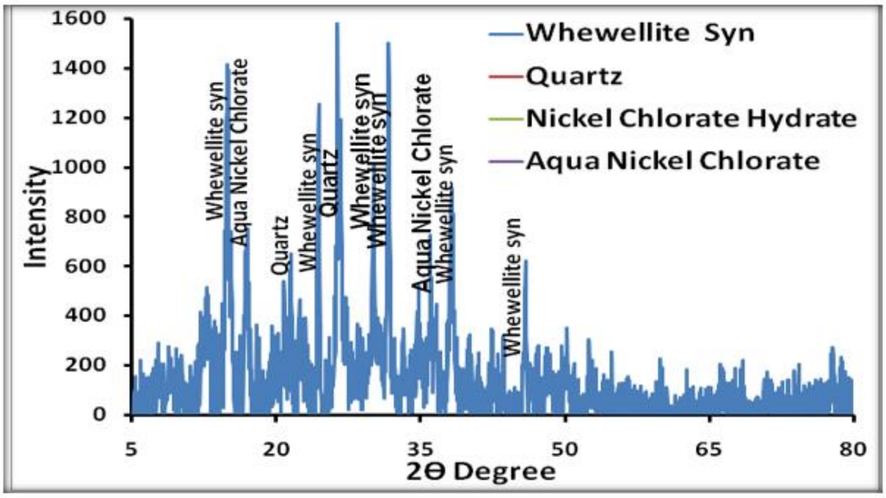

FIGURE 8: Shows XRD For Pulverized Sieved Residue Plantain Peels

The XRD graph displays the minerals in pulverized sieved, unsieved, and sieved residue. The main minerals are whewe elites, quartz, aqua nickel chlorate, and nickel chlorate hydrate (Table 1). The pulverized sieved (Figure 7) and sieved residue (Figure 8) have the highest peak of 1600 with aqua nickel hydrate, while the unsieved (Figure 8) has quartz with the highest peak. The most common peak in the three samples was whewellite syn.

TABLE 1
XRD MINERAL PHASES IN PULVERIZED SIEVED, UNSIEVED, AND SIEVED RESIDUE PLANTAIN PEEL

Mineral Phase	Formula	Number
WhewelliteSyn	$C_2CaO_4.H_2O$ / $CaO_4.H_2O$	00 – 020 – 0231
Quartz	SiO_2	01 – 083 – 0539
Nickel chlorate hydrate	$Ni(ClO_3)_2.6H_2O$	00 – 016 – 0195
Aqua nickel chlorate	$(Ni(H_20)_6\,(ClO_3)$	01 – 079 – 1895

3.4 Adsorption Equilibrium Studies:

3.4.1 Equilibrium Studies on the Effect of Contact Time:

The adsorbent capacity was studied considering the contact time of the solution at the solid/liquid interface. Contact time is an important factor in batch adsorption. Figure 10 shows that the removal efficiency of carbonate and sulphate ions onto the functionalized plantain peel adsorbent increases rapidly in the initial adsorption stage (30-150 min), then slowly until equilibrium is reached after 120 min.

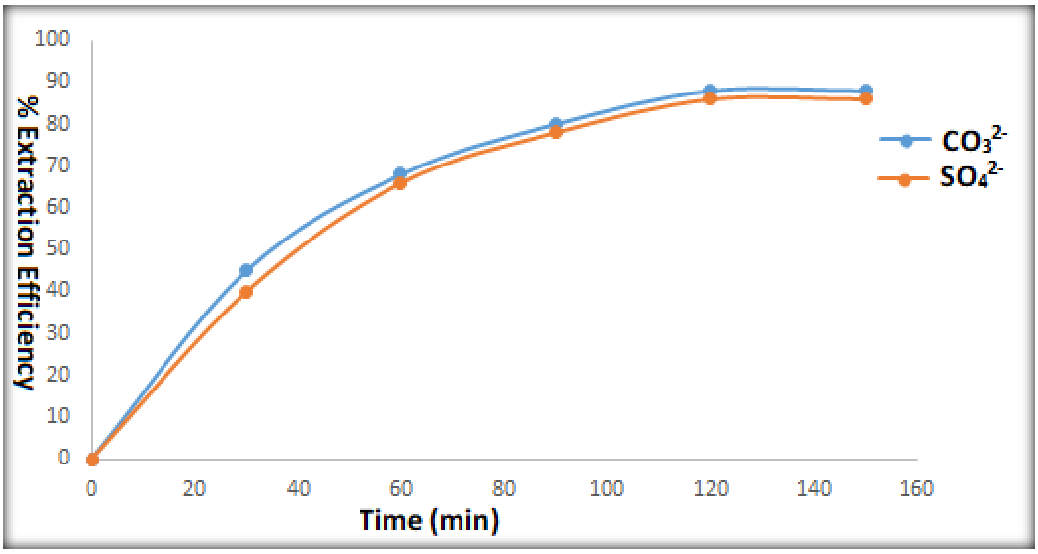

FIGURE 9: Effect of contact time on carbonate and sulfate removal unto functionalized plantain peel

3.4.2 Equilibrium Studies on the Effect of pH

The impact of pH on adsorbate removal (CO_3^{2-} and SO_4^{2-}) by modified plantain peel was studied, as shown in Figure 11. The highest capacities occurred between pH 2 and 4. In acidic conditions, H^+ in the solution increased, making the sorbent surface positively charged, facilitating adsorption of negative anions [19]. The maximum removal of CO_3^{2-} and SO_4^{2-} was 89% and 83% respectively, possibly due to the electrostatic attraction between the acidic proton and the anions.

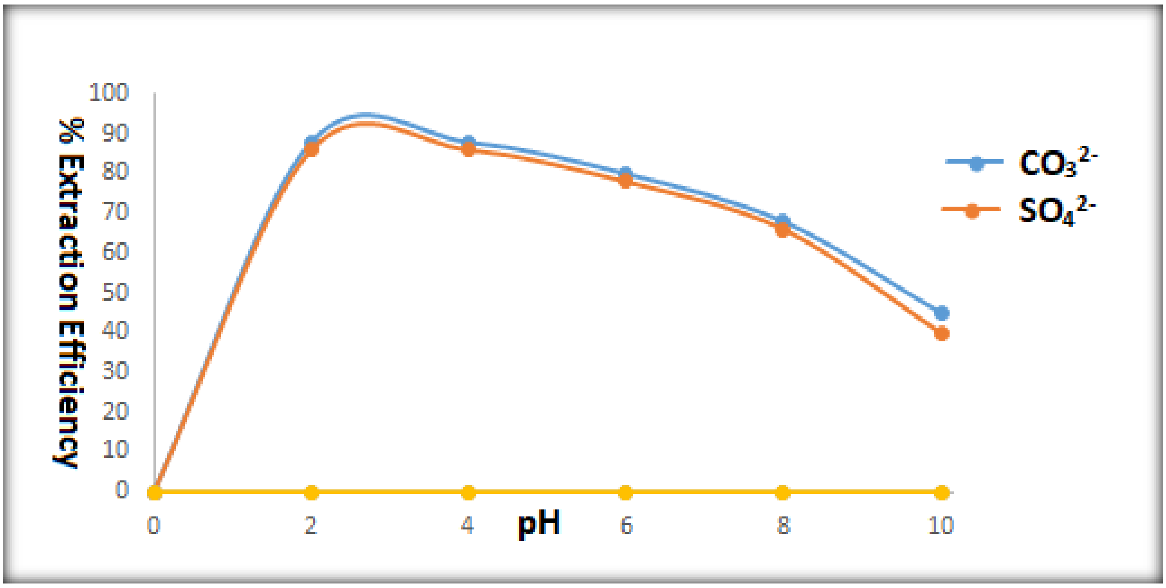

FIGURE 10: Effect of pH of carbonate and sulfate removal unto functionalized plantain peel.

3.4.3 Equilibrium Studies on the Effect of Concentration

Carbonate and sulphate concentrations effect on adsorption rate was studied at pH 4, 29 °C, and 120 min contact time in the range (50-250 mg/L). Figure 12 showed that 150 mg/L had the highest adsorbate removal, reaching equilibrium. The low concentration ratio of initial CO_3^{2-} and SO_4^{2-} ions to fixed sites caused more substances to occupy the interlayer space, reducing ion removal. The highest CO_3^{2-} and SO_4^{2-} removal was 90% and 68% with functionalized plantain peel, respectively.

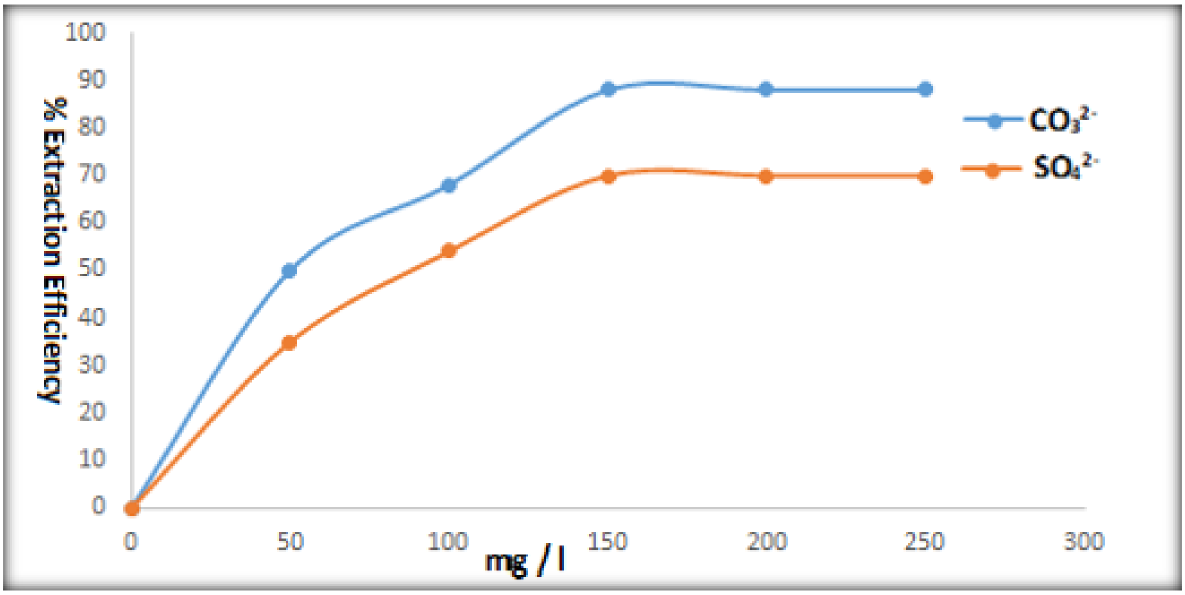

FIGURE 11: The effect of the concentration of carbonate and sulfate removal on unfunctionalized plantain peel

3.5 Adsorption Kinetic Studies

The adsorption kinetics of the adsorption experiments were determined by the pseudo-first-order reaction. The contact time ranges from 30-150 min. the result in Figures 13, and 14 indicate that the experimental data for this study was fitted for a pseudo-first-order kinetic model due to the R^2 value that is closer to the unity.

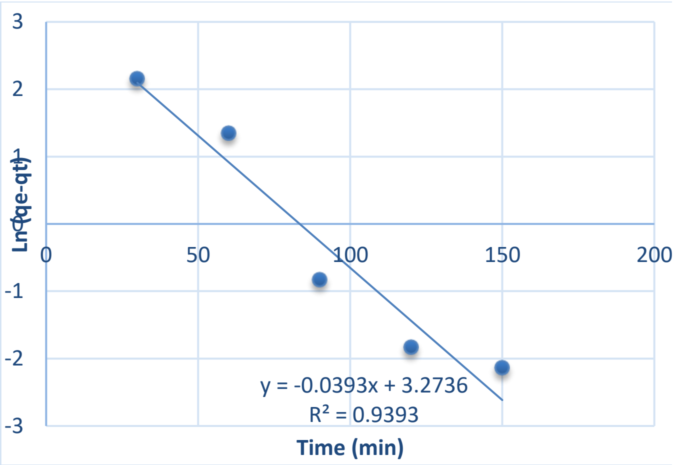

FIGURE 12: Pseudo-first-order kinetics plot for CO_3^{2-}

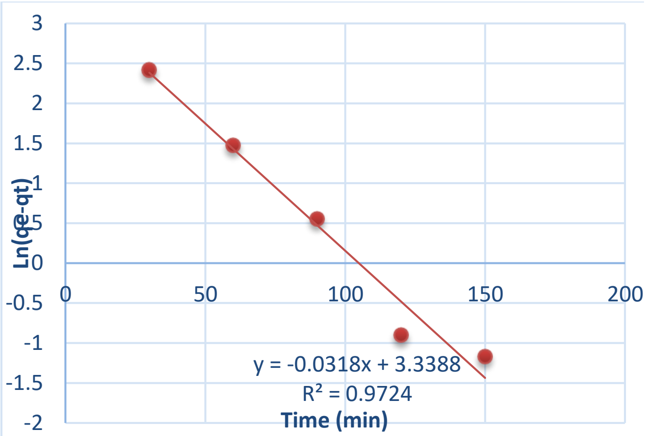

FIGURE 13: Pseudo first-order kinetics plot for SO_4^{2-}

3.6 Adsorption Isotherm Studies

Equilibrium data for adsorption are generally known as adsorption isotherms. In this research, two (2) isotherm models were used: the Langmuir and Frenunlich isotherms applying equations (8) and (10) respectively. Various constants of the models are also calculated and shown in table 2 and 3.

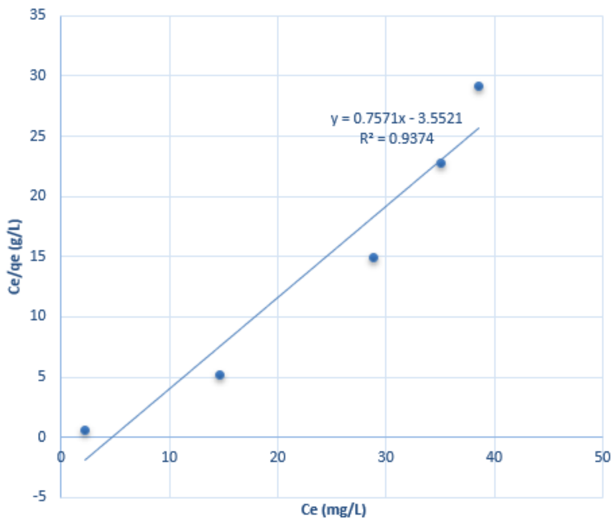

FIGURE 14: Langmuir adsorption isotherm for CO_3^{2-}

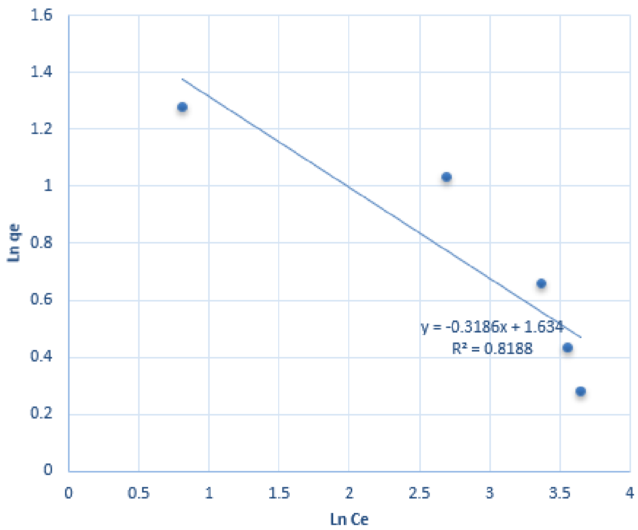

FIGURE 15: Freundlich adsorption isotherm for CO_3^{2-}

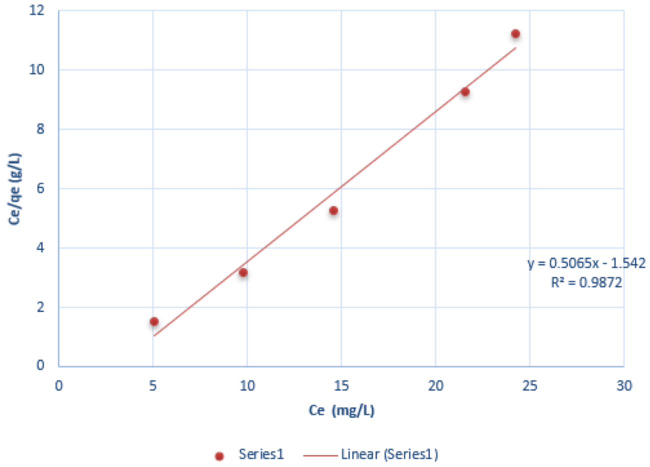

FIGURE 16: Langmuir adsorption isotherm for SO_4^{2-}

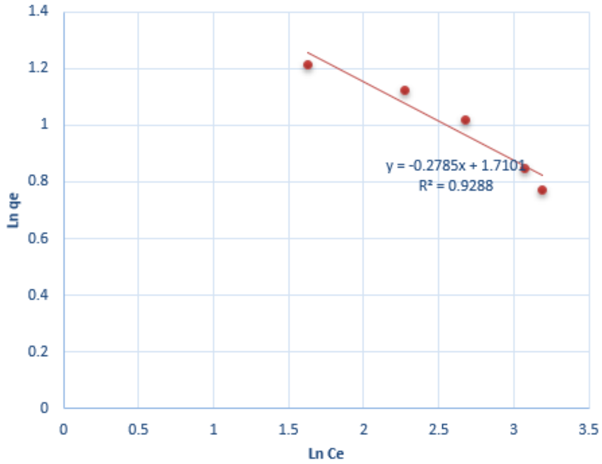

FIGURE 17: Freundlich adsorption isotherm for SO_4^{2-}

TABLE 2

ISOTHERM CONSTANTS FOR CO_3^{2-} ADSORPTION

Langmuir	Values	Freundlich	Values
Q_m (mg/L)	1.867	K_f (mg/Kg)	4.231
K_1 (L/mg)	0.311	N	0.145
R^2	0.987	R^2	0.928
R_l	0.06		

TABLE 3

ISOTHERM CONSTANTS FOR SO_4^{2-} ADSORPTION

Langmuir	Values	Freundlich	Values
Q_m (mg/L)	1.662	K_f (mg/Kg)	3.426
K_1 (L/mg)	0.421	N	0.115
R^2	0.937	R^2	0.818
R_l	0.05		

3.7 Thermodynamic Parameters

The results of the various thermodynamic parameters for the adsorption of CO_3^{2-} and SO_4^{2-} ions are shown in Table 4 and 5 below:

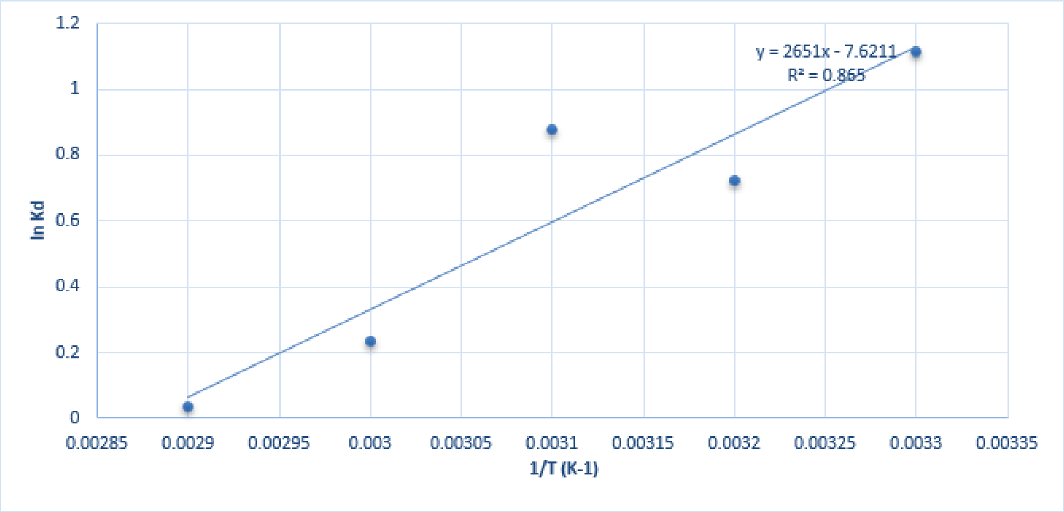

FIGURE 18: Thermodynamics plot for CO_3^{2-}

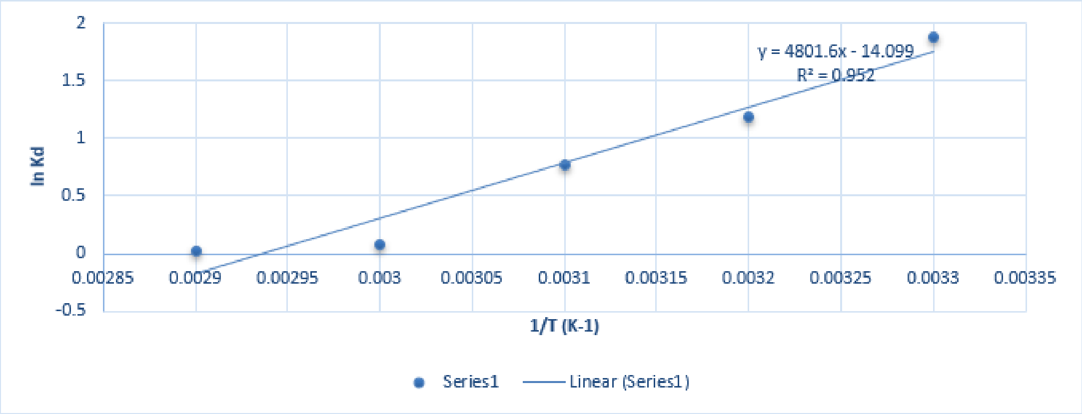

FIGURE 19: Thermodynamics plot for SO_4^{2-}

TABLE 4
THERMODYNAMIC PARAMETERS FOR CO_3^{2-} ADSORPTION

T(K)	LnK	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol/K)
299	1.115	-2.772		
309	0.723	-1.857		
319	0.879	-2.331		
329	1.379	-3.772	-22.04	-63.362
339	0.900	-2.537		

TABLE 5
THERMODYNAMIC PARAMETERS FOR SO_4^{2-} ADSORPTION

T(K)	LnK	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol/K)
299	1.875	-4.661		
309	1.186	-3.047	-39.92	-117.219
319	0.765	-2.029		
329	0.078	-0.213		
339	0.0282	-0.079		

IV. CONCLUSION

Research showed modified natural adsorbents can remove anion pollutants from water, with effectiveness depending on adsorbent dose, temperature, concentration, pH, and contact time. The pseudo-first-order kinetic model and Langmuir model fit the adsorption and equilibrium isotherm data well, respectively. RL values indicated modified plantain peels were suitable for anion adsorption. Thermodynamic analysis revealed the reaction was spontaneous, exothermic, and physisorption. Thus, modified plantain peels are a promising, low-cost adsorbent for carbonate and sulphate ion removal from aqueous solutions.

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