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Research Article

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Special Issue
A Themed Issue in Honour of Professor Onukwuli Okechukwu Dominic (FAS).

This special issue is dedicated to Professor Onukwuli Okechukwu Dominic (FAS), marking his retirement and celebrating a remarkable career. His legacy of exemplary scholarship, mentorship, and commitment to advancing knowledge is commemorated in this collection of works.

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Adsorptive Removal of Azo Dye from Aqueous Solution Using Sustainable Material: Equilibrium, Kinetic, and Optimization Analysis.

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Abstract

Dyes are colored substance of environmental concern due to their negative impacts on the water quality of both surface and ground water. This research focused on removal of Congo-red dye (CR) from effluent using the adsorptive qualities of Awka raw clay (ARC). The batch system was applied to evaluate the effect of process-independent variables. The thermodynamic properties ΔS, ΔH, ΔG, and Ea were determined. The optimum CR removal was predicted using the RSM model. Maximum percentage dye removal and adsorption capacity of 66% and 26.41 mg/g respectively were obtained via batch adsorption system. Thermodynamic results confirm the CR adsorption as endothermic, spontaneous, and physical process. The RSM model, with R2 of 0.9982 confirmed the model prediction statistically accurate. These obtained results confirm ARC cost-effective adsorbent for CR removal from effluents.

Keywords: adsorption, dye, equilibrium, kinetic, modeling, thermodynamics

1. Introduction

The societal shift from an agricultural-based to an industrial economy has led to significant pollution challenges in both developed and underdeveloped countries. The transition in the economy has positively benefited mankind but negatively affected the ecosystem (aquatic and terrestrial environments). High rate of pollution is attributed to poor waste management and poor implementation of environment laws regulating the discharge of sewage and solid waste. Among the many sources of pollution, water pollution has been of most concern due to high-rate wastewater generation of different contaminant concentration (Oguanobi et al. 2024b). Recently, different physico-chemial, chemical, physical, and biological treatment techniques such as coagulation and flocculation, sonochemical degradation, adsorption, photochemical degradation, electrochemical removal, membrane separation, anaerobic sequential process fento-biological treatment scheme etc. have been explored in trying to minimize the trait of water pollution from the point source (Oguanobi et al. 2024b). However, adsorption has been prioritized or most adopted techniques due to the advantage of completely removal of color from wastewater (Oguanobi et al. 2024a).

Adsorption is the adhesion of molecules, ions, and atoms from a liquid, dissolved solid, or gas to the surface of a material called an adsorbent. Different non-conventional adsorbents have been exploited due to the limitation of high operating costs of the conventional adsorbent (activated carbon), and all show the capacity to replace conventional activated carbon. Some of the previously exploited non-conventional adsorbents include modified clays (Oguanobi et al. 2018, Nayoon et al. 2022, Oguanobi et al. 2024a), biomass (Mohammed et al. 2023, Zhi et al. 2022), agriculture waste (Dal and Meenal 2022, Onu et al. 2020), etc. However, clays have been preferred non-

conventional exploited adsorbent to replace conventional activated carbon due to its ability to adsorb ions and molecules on both external and interlayer particle sites.

Response surface methodology (RSM) is a model used to generate a mathematical model that can satisfactorily give the optimum parameters for operating a process. It helps in the simultaneous examination of process variables that affect a process, even in the presence of complex interactions. RSM only needs small experimental runs to predict an optimum condition. Therefore, the purpose of the current work was to evaluate the influence and the adsorptive capabilities of ARC through removal of Congo red dyes from aqueous solution and also using optimization model (RSM) in predicting the optimum condition for removal of CR dye from wastewater. Hence the novelty of the work lies on the application of optimization methods to predict the optimum conditions for CR removal from effluent using ARC adsorbent.

2.0. Materials and methods

The major raw material used is milk-colored clay sourced from Okpuno village in Awka South Local Government Area of Anambra State, Nigeria, while all secondary raw materials utilized are analytical grade and purchased from Head Bridge Market in Onitsha, Anambra State. All of the solutions were made with distilled water.

2.2 Characterization

The raw clay samples were tested to determine the functional group and surface morphologies. The functional group analysis, commonly known as Fourier transform infrared (FTIR) analysis, was performed using the Shimadzu spectrophotometer model S8400 and samples prepared using the traditional KBr disc method. The surface morphology examination, commonly known as scanning electron microscopy (SEM) analysis, was performed with the Joel scanning electron microscope model JSM 6400 and a coated gold film of layers around 20-25 A thick.

2.3 Batch Adsorption Studies

Batch adsorption studies were studied to examine the process effects of adsorbent particle size, adsorbent dose, initial dye concentration, contact time, and pH on CR uptake on raw clay adsorbent. A CR solution was prepared by dissolving a known quantity of dye crystal in distilled water. The solution obtained was used as a stock solution and diluted to the required initial concentration range of 100 to 300 mg/L. The pH adjustment of the solution was achieved by using either 0.1N HCl or NaOH. The resulting effect of the studied process variables on CR uptake was determined using a UV-visible spectrophotometer.

2.4 Equilibrium/isotherm studies

The adsorption equilibrium experiment was carried out by contacting a predetermined quantity of adsorbent into glass beakers (200 ml) holding a specific volume of varying concentrations of CR dye solution with the same pH level. These beakers containing the mixture or solution were placed on shakers (magnetic stirrers) set at a predetermined temperature for 75 minutes to guarantee equilibrium was reached. A UV-visible spectrophotometer is used to estimate the equilibrium concentration of the dye. At equilibrium, dye uptake "qe" (mg g^{-1}), was evaluated using expression of equation 1

$$qe = \frac{(C_o - C_e)V}{m} \quad (1)$$

Percentage dye uptake was evaluated using equation 2.

$$\% \text{ Adsorption} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where C_o and C_e(mg L^{-1}) were initial and equilibrium dye concentrations respectively, while V and m were the volume of the solution in liter and the mass of dry sorbent in gram. Two isotherm models were used to fix the equilibrium data: the Langmuir and the Freundlich, with their non-linearized expression in equations 3 and 4. The parameters of each model provide vital information on the adsorption mechanisms, surface properties, and adsorbent affinity.

Langmuir adsorption isotherm: Langmuir isotherm expression describes adsorption homogeneity (homogeneous adsorption) as a process where all active sites have even energies and indistinguishable affinity for adsorbate onto

the surface without the migration of molecules between localized surfaces. The non-linearized form of the Langmuir model can be expressed as follows:

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

Where q_m (mg/g) is Langmuir adsorption capacity constants, K_L (L/mg) is Langmuir energy/affinity of adsorption constants, C_e (mg/L) is the equilibrium concentration, and q_e (mg/g) is the amount of dye adsorbed at equilibrium. The essential feature of the Langmuir isotherm was expressed by means of R_L, a dimensionless constant referred to as the separation factor or equilibrium parameter. R_L is calculated using the expression of equation 3b.

$$R_L = \frac{1}{1 + K_L C_o} \quad (3b)$$

The value of R_L classifies the adsorption process into the following categories: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Freundlich adsorption isotherm: The Freundlich isotherm explains the relationship between the pressure or concentration of the adsorbate at a constant temperature and the quantity of adsorbate adsorbed onto an adsorbent (a solid surface). The non-linearized form of the Freundlich model can be expressed as follows:

$$q_e = K_F C_e^{\,1/n_F} \quad (4)$$

Where C_e (mg/L) is the equilibrium concentration, q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, K_F is Freundlich adsorption capacity and affinity constants, and n is the Freundlich adsorption intensity and mechanism constants, $1/n_f$ is a measure of the surface heterogeneity of the adsorption site.

2.5 Kinetic Studies

In kinetic experiments, aqueous samples were taken at different time intervals to determine the uptake of dye at any preset time t. At time t, dye uptake "qt" (mg g^{-1}) was evaluated using equation 5.

$$qt = \frac{(C_o - C_t)V}{m} \quad (5)$$

Where C_t is dye concentration at any time t.

In this research work, three kinetic models were employed: the pseudo-first order, the pseudo-second order, and intra-particle diffusion. The intra-particle diffusion is proposed to identify the rate determining step of the adsorption.

Pseudo-first-order model (PFO): The pseudo-first-order kinetic model is an empirical method used to analyze the rate of a chemical reaction or other process. The model is called "pseudo" because it may not precisely replicate a true first-order reaction, but rather, it is a simplified approach used to estimate the reaction kinetics. The non-linearized form of the pseudo-first-order model can be expressed as follows:

$$q_t = q_e[1 - exp(K_1 t)] \quad (6)$$

Where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, q_t (mg/g) is the amount of adsorbate adsorbed at time t. K_1 (min^{-1}) is the adsorption rate constants for pseudo-first-order.

Pseudo-second-order model (PSO): The pseudo-second-order model is an extension of the conventional second-order kinetic model, and it gives more detailed knowledge to chemical systems where the reaction rate depends on the surface coverage of adsorbed species. The non-linearized form of the pseudo-first-order model can be expressed as follows:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (7)$$

Where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, q_t (mg/g) is the amount of adsorbate adsorbed at time t, K_2 $gmg^{-1}min$ were the adsorption rate constants pseudo-second-order.

2.6 Adsorption Thermodynamics

Thermodynamics studies were to determine the energy changes involved in the adsorption. Thermodynamic parameters are determine using the following equations.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

$$\Delta G^o = -RT \ln K_c \quad (9)$$

Where $K_c = \frac{C_s}{C_e}$ (10)

$$\ln K_c = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \quad (11)$$

Where ΔG^o, ΔH, ΔS are the standard; Gibbs free energy change, enthalpy change (heat of reaction) and entropy change, respectively. K_c is the equilibrium constant, C_s is the equilibrium concentration of CR on solid (adsorbent (mg/L)), R is the general gas constant (8.314J/mol/K) and T is adsorption temperature on Kelvin scale.

2.6.1 Activation energy

The nature of adsorption process can be inferred from the level of activation energy. The Arrhenius rate expression of equations 12 and 13 were used to evaluate the activation energy of adsorption.

$$K_A = Ae^{-Ea/RT} \quad (12)$$

$$InK_A = InA - \frac{Ea}{RT} \quad (13)$$

Where Ea is the Arrhenius activation energy (KJ/mol) K_A is a pseudo-second-order rate constant of adsorption (g/mg min), R is the universal gas constant (8.314J/molK) and T is the absolute solution temperature (k). Ea Can be calculated from the plot of InK_A versus 1/T.

2.7 RSM modeling

Design expert version 13 was used in both the design and the RSM-CCD analysis. The experiment was designed using a central composite design (CCD) with five factor levels. RSM uses data obtained from design of experiments and statistical modeling technique to solve multi-variant problems (Venkatesh and Karthikeyan 2018).

The independent variables used were temperature, pH, concentration and time whereas the actual response (percentage adsorbed) was the dependent variable.

The number of data sets for RSM-CCD experiment can be evaluated using expression of equation 21 (Arulkumar et al. 2011).

$$Q = 2^q + 2q + q_c \quad (14)$$

Where q is the number of input factors and 2^q, 2q and q_c represents the: factorial points, axial points, and center points.

3.0 Results and Discussion

3.1 Characterization Result

3.11 FTIR analysis

Figure 1 presents the FTIR of raw Awka clay (RUC). The spectra show good characteristics of adsorption peaks for binding of CR dye e.g. Amide, alkane, alcohol, alkyne halide at the functional region. The observe peaks in the spectra were all strong broad and sharp peaks of both polar groups (O-H, N-H, and C=O strech) and non-polar groups (C=C and C≡C strech). The presence of some functional groups at the finger print region like the peak at 1032 cm^{-1} which represent the C-O stretch of carboxyl group (ether or ester) can also support adsorption of CR dye.

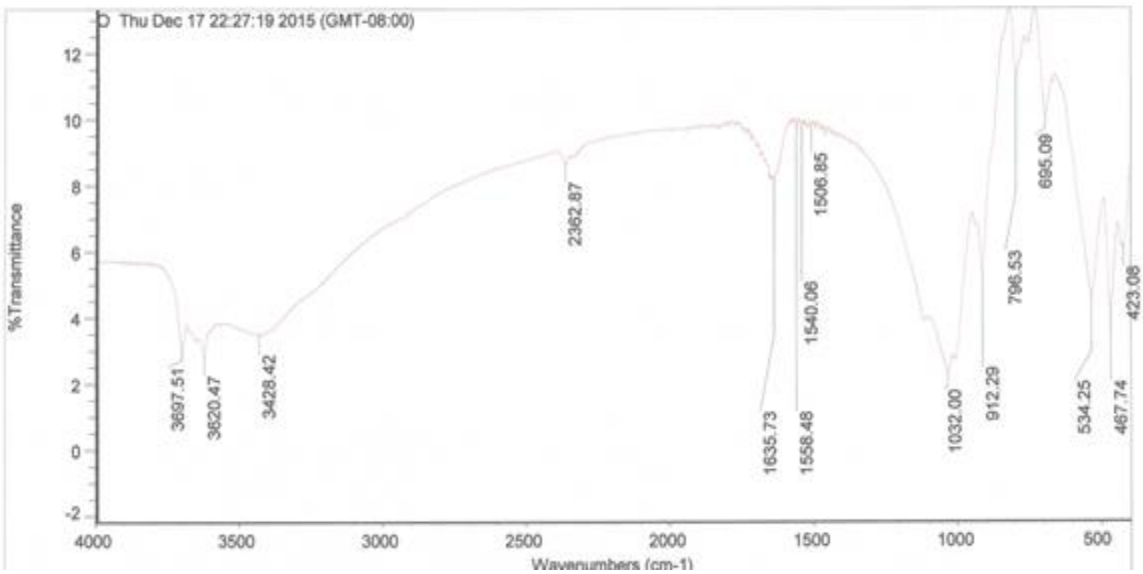


Figure 1 FTIR spectra of Awka raw clay.

3.12 SEM micrographs

Figure 2a and b present the scanning electron micrograph (SEM) of the Awka raw clay sample and after CR adsorption on the ARC sample. Figure 2a clearly displayed a considerable number of heterogeneous layers of pores and the internal surface of the clay material. Figure 2b showed a decreased number of heterogeneous layers of pores with a smoother and brighter surface, which is attributed to adsorption taking place on the adsorbent surface. The observed smooth and bright surface is dye particles that cover most porous surfaces of Figure 2a.

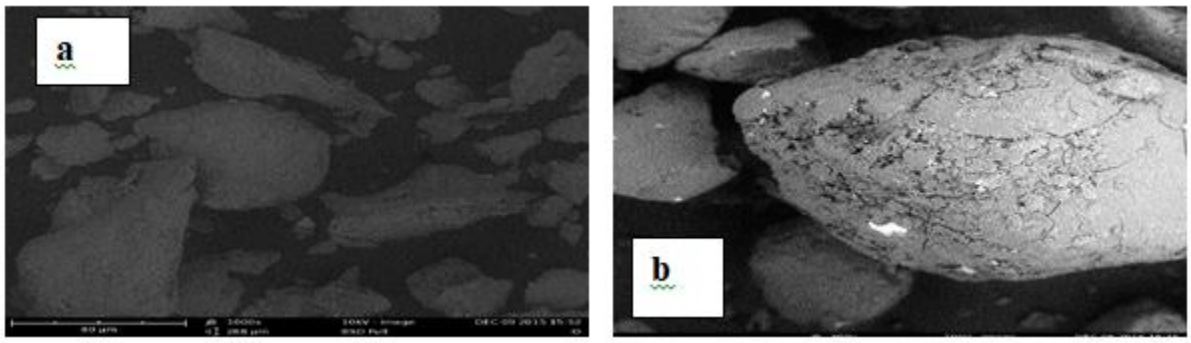


Figure 2. SEM Micrograph of: (a) raw clay, (b) after adsorbed clay

3.2 Batch Adsorption Results

3.21 Effect of Adsorbent Dosage

The impact of adsorbent dosage was studied at the dosage range of 0.1, 0.2, 0.3, 0.4, and 0.5 g at a constant temperature of 323 K, an adsorbent particle size of 75 µm, a pH of 2, an initial ion concentration of 100 mg/l, and a time of 60 min. The result as reported in Figure 3a shows an increase in adsorption percentage as dosage increases, from 26.8% at 0.1 g to 64.7% at 0.5 g. The notable increase in CR percentage adsorption as adsorbent dosage increases is attributed to the increased surface area of active functional groups, which also gives rise to a greater availability of adsorption sites (Ismat et al. 2023; Imessaoudene et al. 2023; Oguanobi et al. 2024e).

3.22 Effect of Particle Size

The effect of particle size was studied with particle sizes range from 75 to 850 µm at a constant temperature of 323 K, an adsorbent dosage of 0.5 g, a contact time of 60 min, pH of 2, and an initial ion concentration of 100 mg/l. The result as reported in Figure 3b shows an increase in percentage CR adsorption as adsorbent particle size decreases,

i.e., from 17.6% at 850 µm to 65.7% at 75 µm. This is attributed to the fact that smaller particles possess a larger surface area and pores than bigger particle sizes (Oguanobi et al. 2018; Oguanobi et al 2024c).

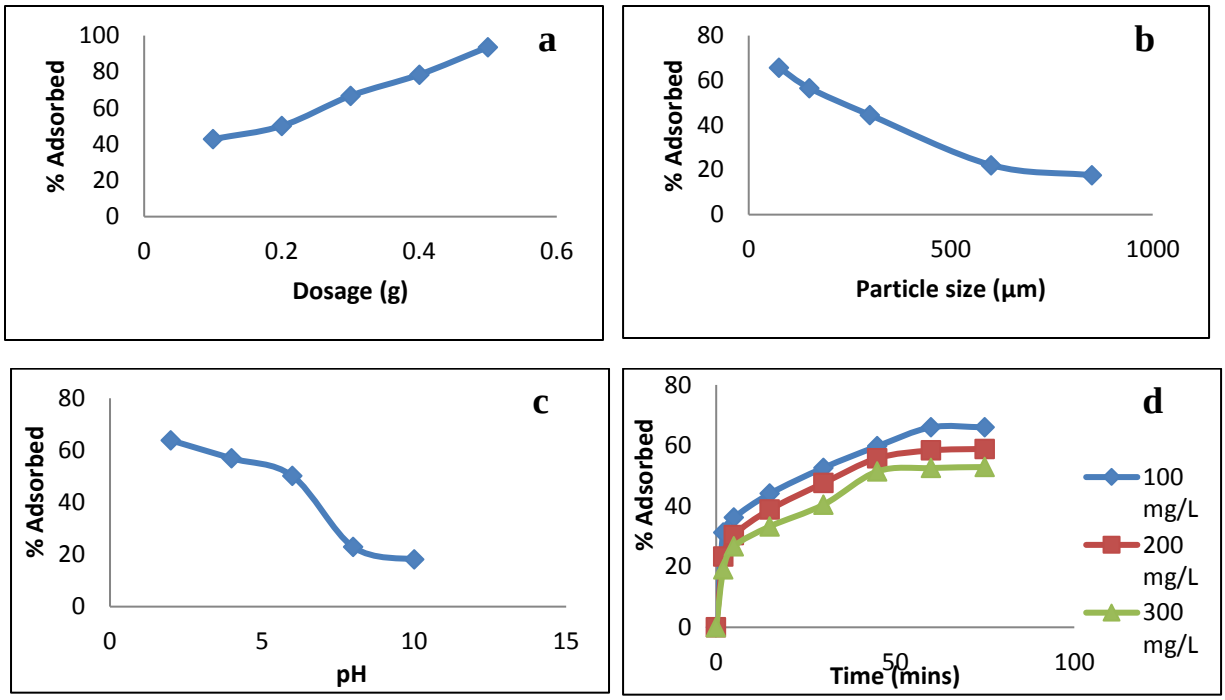


Figure 3. Effects of process variable displaying impact of (a) dosage, (b) particle size, (c) pH, and (d) initial concentrations and time on the percentage of CR adsorbed

3.23 Effect of pH

The pH effect is studied between the pH ranges of 2 and 10, at a temperature of 323 K, an adsorbent particle size of 75 µm, a time of 60 min, an adsorbent dosage of 0.5 g, and an initial ion concentration of 100 mg/l. The result as reported in Figure 3c shows that the highest removal efficiency of 63.9% was achieved at pH 2. This is attributed to the very low solubility of CR at pH < 2. At low pH the clay adsorbent acquires a positive charge by adsorbing H^+ ions, and this leads to significantly strong electrostatic attraction between the positively charged sites and the anionic dye molecules. This finding concurs with previous reports by Imessaoudene et al. (2023) and Oguanobi et al. (2024b).

3.24 Effect of Concentration and Contact Time

The effect of initial ion concentration was investigated between the concentration ranges of 100–300 mg/l at a 0.5 g adsorbent dosage, a contact time of 75 minutes, a temperature of 323 K, a pH of 2 and an adsorbent particle size of 75 µm. The result as reported in Figure 3e shows an increase in the amount of CR adsorbed per unit mass of adsorbent as initial ion concentration increases from 100 to 300 mg/l, whereas the adsorption percentage decreased. This is attributed to the proportion of the initial number of dye molecules to the available surface area at low concentration. Moreover, an increase in the quantity or percentage of adsorption as contact time increases at all initial concentrations until equilibrium was observed. This is attributed to the fact that more CR molecules have the opportunity to transfer and diffuse into the adsorbent surface as contact time increases (mass transfer and diffusion). The findings are consistent with those of Barakan et al. (2019) and Oguanobi et al. (2018).

3.3 Equilibrium Modeling

The equilibrium adsorption presents the correlaction between the mass of adsorbate adsorbed per unit weight of adsorbent and the liquid-phase equilibrium concentration of the adsorbate.

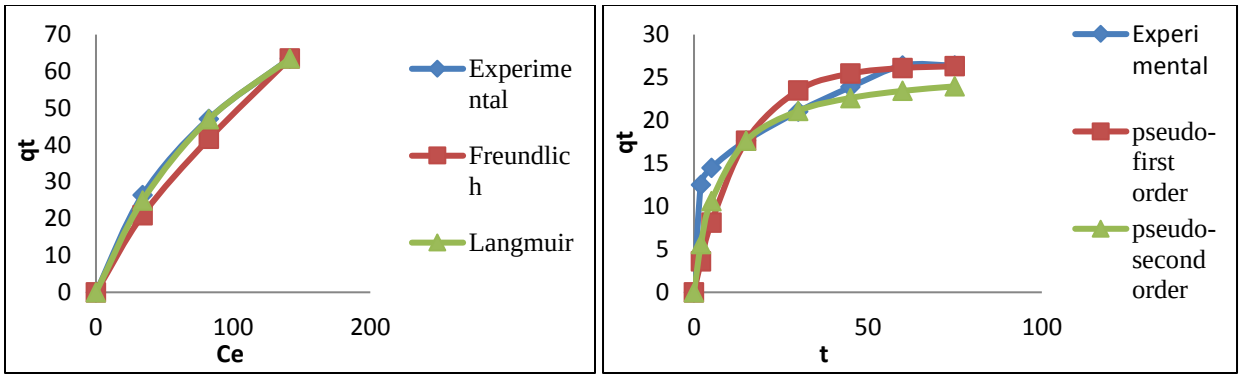


Fig.4. Non-linear plot of: (a) isotherm and (b) kinetic models for adsorption CR on ARC.

The obtained Langmuir maximum adsorption capacity (q_m) value is 124.3 mg/g and the K_L Value of 0.007385 indicates strong affinity of the adsorbent surface for adsorbate molecules. The R_L value of 0.4894 confirms favorable uptake of CR dye (strong adsorption).

Table 1: Isotherm and Kinetic Parameters for CR adsorption on ARC

Langmuir	Feundlich	PFO	PSO
			qe exp = 12.9998
K_L= 0.007385	KF= 1.3531	K_1 = 0.07342	K_2 = 0.005138
qm = 124.3	nf = 1.2865	R^2 = 1	R^2 = 1
R_L = 0.4894	R^2 = 1	qe = 26.4311	qe = 26.3369
R^2 = 1	NSD = 3.9666	Ho = 1.9405	Ho = 3.5638
NSD = 0.5856		NSD = 2.6729	NSD = 2.1759

The Freundlich equation is an empirical relationship between the amounts of adsorbate adsorbed onto adsorbent. The n_f value of 1.2865 confirms that the adsorption sites have uniform energies and thus classify the surface as more homogeneous. Moreover, the n_f value also confirms CR dye adsorption a favorable and physical process.
The high q_m value of Langmiur validates the results of parameters K_L *and* n_f which confirm the good affinity of the adsorbent for the adsorbate.

3.4 Kinetic Modeling

The PFO and PSO non-linear kinetic expressions were used to fit the experimental data of adsorption kinetics of CR onto ARC. The pseudo-kinetic model presumes that adsorption process is a pseudo-chemical reaction. The curve fittings of the models are presented in Figure 5, and the values of their constants were evaluated using Excel software and tabulated in Table 1. The K_1 value of 0.07342 for PFO suggests a slow adsorption process, whereas the small K_2 value of 0.005138 for PSO confirms zero correlation with the dye initial concentration, thus indicating that more than one adsorption mechanism controls the adsorption of CR. The H_o constant of PFO and PSO calculates the initial adsorption rate, and pseudo-first-order Ho value of 1.9405 and the pseudo-second-order Ho value of 3.5638 concur with the experimental data. The PFO and PSO models qe calculated values of 26.4311 and 26.3369, respectively, conform to experimental qe (26.4052).

3.5 Error Function Statistical Analysis

The equilibrium and kinetic models best fit assessment for the removal of CR dye on ARC was evaluated using the normalized standard deviation (NSD) error parameter of the non-linear regression expression of equation 15.

$$NSD = 100 \times \sqrt{\frac{\sum_i^N [(q_e \exp - q_e cal)/q_e exp]^2}{N-1}} \qquad (15)$$

Where N is the number of experimental runs; $q_{e,exp}$ and $q_{e,cal}$ are the experimental values and model calculated values respectively.

The non-linear regression rule for goodness of fit assessment is the smaller the value of the error function, the better the curve fits. The results of the studied error function for equilibrium and kinetic models, as tabulated in Table 1, show that the Langmuir model gives the best fit to the experimental isotherm data, whereas the PSO kinetic model gives the best fit to the experimental kinetic data because the NSD value is lower for PSO than PFO model. This is attributed to small deviation value between predicted and experimental value.

3.6 Thermodynamic Study

The plot of Figure 5b depicts In KC versus T^{-1} of the CR adsorption process. The slope and intercept obtained from curve-fitting are utilized to determine the ΔH and ΔS values.

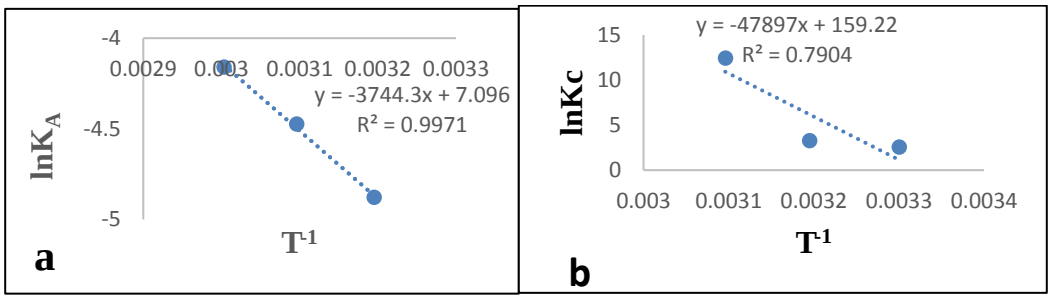


Figure 5a and b, Plot of InK_A and InK_c against T^{-1} for the removal of CR by clay adsorbent

The slope of the plots equal to -ΔH°/R and its intercept is equal to ΔS°/R. The calculated parameters of ΔG, ΔH and ΔS are shown in Table.2.

Table 2 Thermodynamics parameters for the adsorption of CR on ARC

Temp (K)	ΔG (KJ/mol)	ΔS (J/mol)	ΔH (KJ/mol)	E_a (KJ/mol)
303	-201.629			
313	-635.938	78.29876	23634.208	15.14229
323	-1782.77			

The negative ΔG values signify that adsorption is spontaneous which implies that the process occurs naturally without an external force, and the kinetic significance of spontaneity process is fast adsorption rate and adsorbent high affinity for the adsorbate, whereas the practical implication is that the adsorbate is unlikely to leach or desorb back into the solution and easy efficient separation of component in the mixture. Moreover, the decrease in the obtained result of ΔG values as the temperature increases indicates that an increase in temperature favors the adsorption of CR on ARC. The positive ΔH value indicates that the adsorption process is endothermic, and the positive ΔS value suggests increased randomness at the solid or solution interface during the adsorption of CR on ARC and corresponds to an increase in the degree of freedom of the adsorbed species. The E_a value, as seen in Table 2, is positive and less than 40 KJ mol^{-1}, thus indicating that adsorption of CR using ARC is feasible and a physical process. A similar result of the same trend was reported on the adsorption of crystal violet on RAC (Oguanobi et al. 2024a).

3.7 Modeling Using Response Surface Methodology

The quadratic model for prediction the optimum point of CR adsorption was suggested from the CCD module with R-squared of 0.9982, adjusted R^2 of 0.9967 and predicted R^2 of 0.9856. Table 3 presents the analysis of variance (ANOVA) and it confirmed the adequacy of the quadratic model.

Table 3: ANOVA and model coefficients for CR adsorption

Source	Sum of squares	df	Mean squares	F-value	p-value Prob>F
Model	189.29	9	21.03	632.21	< 0.0001
A-pH	1.02	1	1.02	30.58	0.0003
B-Dosage	11.44	1	11.44	343.87	< 0.0001
C-Concentration	10.76	1	10.76	232.57	< 0.0001
AB	67.51	1	67.51	2029.31	< 0.0002
AC	0.3200	1	0.3200	9.62	0.0112
BC	19.78	1	19.78	594.62	< 0.0001
A^2	5.82	1	5.82	175.05	< 0.0001
B^2	9.51	1	9.51	285.94	< 0.0001
C^2	71.45	1	71.45	2147.75	< 0.0001
Residual	0.3327	10	0.0333		
Lack of fit	0.3327	5	0.0665		
Pure error	0.0000	5	0.0000		
Cor total	189.63	19			

The F-values and P-values are used to check significant terms of the model. The smaller the P-value, the higher the F-value and the more significant the corresponding coefficient. The model F-value of 632.21 implies that the model is significant, and P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. A similar trend was reported by Oguanobi et al. (2024b). The relationship between the response and independent variable in coded form based on the experiment results was reported as follows:

$$\text{Percentage Adsorbed, } = +96.75 + 0.2730A + 0.9153B - 0.8878C - 2.90AB - 0.2000AC - 1.57BC - 0.6357A^2 - 0.8125B^2 - 2.23C^2 \quad (16)$$

The good fit of the model equation was confirm using R-square. The high coefficient of regression value of 0.9982 implies that 99.8% of the variability in the response can be explained by the model. Moreover, the obtained high coefficient of regression value implies that the model can accurately predict or forecast future outcomes based on the input variables and the model can as well help in pinpoint or singling out the most important variables and their relationship for improved productivity and efficiency.

3.71 RSM graphical plots

The 3D surface plots represent the effect of two process variables on the adsorption of CR. Figure 6a-b, presents the relationship between every two independent process variables. The parabolic nature of the contour in the graphs shows that there was a perfect significance between two variables.

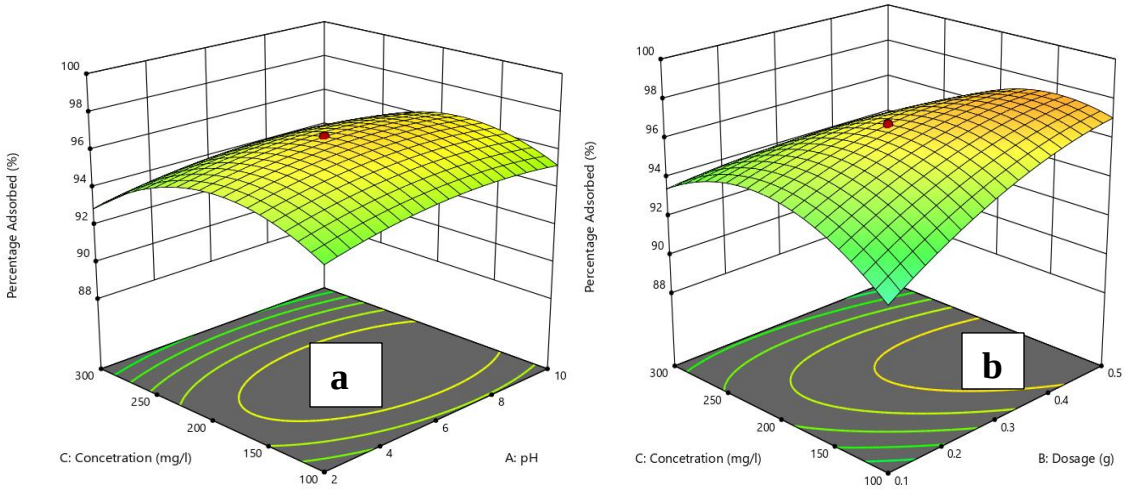


Figure 6. 3D surface plot for CR adsorption on ARC showing combined effects of (a) Concentration and pH, (b) Concentration and Dosage

Figure 6a shows that decrease in: concentration from 300 mg/l to 100 mg/l and in pH from 10 to 2 led to increase in dye percentage removal whereas Figure 6b shows that increasing dosage from 0.1 g to 0.5 g and decrease in concentration also increases CR percentage removal.

3.8 Comparative Performance of the Adsorbent

A comparison of the adsorption of CR dye with other adsorbents was made to ascertain the efficiency and relevancy of the raw clay used in this study. Maximum adsorption capacity (q_{max}), percentage removal, and adsorbent dosage were the parameters utilized in the comparison, as shown in Table 4.

Table 4: Comparison with other adsorbents

Adsorbent	Adsorbent dos (g)	Removal eff (%)	Ads capacity(mg/g)	Adsorbate	Reference
Pottery clay	0.05	94.75	1.086	Congo red	Baydaa and Lekaa (2022)
MgAl-LDH	0.05	60	769.23	Congo re	Mohamed et al. (2022)
PDFe/Al	1	99	411	Congo red	Khathutshelo et al. (2022)
GlARConite	0.02	80	11.9	Congo red	Hamd et al. (2023)
Treated clay	0.3	90	39.80	Heavy metals	Paul and Mutsee (2021)
Raw clay	0.5	64.99	25.99	Crystal violet	Oguanobi et al. (2024a)
Banana stem	0.5	87	14.28	Remazole red	Kumar et al. (2022)
Rice bran	2	97.4	603	Crystal violet	Mojtaba et al. (2020)
Fe-bent	2	99	10.06	Arsenic(v)	Barakan et al. (2019)
RIC	0.5	68.78	27.5	Congo red	Oguanobi et al. (2024d)
Activated carbon	0.04	95	658	Crystal violet	Alkhabbas et al. (2023)
Biochar	0.5	68	20.23	Rhodamine B	Ibrahim et al. (2021)
ARC	0.5	66.01	26.41	Congo red	Present study

Table 4 shows that ARC has higher adsorption capacity and removal efficiency than some of the reviewed adsorbents. The availability of this clay in a large deposit in Awka town, Nigeria, with its adsorption efficiency, makes it a viable, effective, and alternative adsorbent in the removal of CR from aqueous solution.

4.0 Conclusions

The current study demonstrated the potential of ARC as an adsorbent for dye removal from aqueous solutions. The adsorption of CR onto ARC was found to be dependent on the pH, initial ion concentration, adsorbent dosage, adsorbent particle size, and contact time. The equilibrium data was best described by the Langmuir model, whereas the kinetics data was best represented by the PSO model. The Langmuir model maximum adsorption capacity (qm) value of 124.3 mg/g was obtained. The thermodynamic studies certified CR adsorption as a spontaneous, endothermic, favorable, and physical process. The RSM model predicted optimum adsorption of 98.88% under the optimum conditions and process parameters (100 mg/l initial dye concentration, 0.5 g dosage, and pH of 2). Finally, for the fact that that RSM model satisfactorily generate a quadratic equation to accurately predict or forecast future outcomes based on the input variables and the other results of the study confirming ARC as reliable and cost-effective adsorbent for CR removal from effluents, suggestion for future research is recommended on reusability of the adsorbent (ARC) since the thermodynamic study suggested spontaneous process of which the practical implication is efficient separation of component in the mixture.

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