

Equilibrium, Kinetic, and Thermodynamic Study of The Adsorption of Cu(II) From Aqueous Solution Using Activated Carbon Derived From *Acacia*

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دراسة التوازن والحركية والديناميكا الحرارية لامتنزاز النحاس الثنائي من محلول مائي باستخدام الكربون المنشط المشتق من الأكاسيا

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Abstract

The mechanism of adsorption behavior of thermally activated carbon prepared from *Acacia* (AAC) for copper ions from aqueous solutions has been investigated at optimum conditions of removal in a batch system. The experimental data were analyzed by the Langmuir, Freundlich, Timken, and Dubinin-Zaverina-Radushkevich adsorption isotherm models of adsorption. The characteristic parameters for each isotherm and related coefficients of determination have been determined. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° have also been evaluated. The kinetics of the sorption were analyzed using the Simple First Order, pseudo-first-order, pseudo-second-order, and Intra-Particle Diffusion kinetic models. Kinetic parameters, rate constants, equilibrium sorption capacities, and related coefficient of determination for each kinetic model were calculated and discussed. It was shown that the adsorption of copper could be described by the pseudo-second-order model, and it has been found that the adsorption process was feasible, spontaneous, and endothermic, suggesting that the adsorption process is presumably chemisorption. The AAC investigated in this study showed good potential for the removal of copper from aqueous solutions. So, the present study shows the feasibility of the practical use of AAC as a low-cost, and natural material adsorbent for the effective removal of Cu(II) ions from aqueous solutions as an alternative to existing commercial adsorbents.

Keywords: Copper; *Acacia*; Equilibrium; Kinetic; Thermodynamic, Adsorption.

الملخص

تمت دراسة آلية سلوك الامتنزاز للكربون المنشط حرارياً المحضر من الأكاسيا (AAC) لأيونات النحاس من المحاليل المائية في الظروف المثلى للإزالة باستخدام النظام الدفعي. تم تحليل البيانات التجريبية بواسطة نماذج الامتنزاز (لانجموير وفريوندليش وتيمكين ودوبينين- زافيرينا-رادوشكيفيتش). تم تحديد المعلمات المميزة ومعاملات التحديد ذات الصلة عند درجات الحرارة بنطاق الدراسة. تم أيضاً تقييم المعلمات الديناميكية الحرارية [ΔG° و ΔH° و ΔS°]. كما تم تحليل حركيات الامتنزاز باستخدام النماذج الحركية من الدرجة الأولى البسيطة، ومن الدرجة الظاهرية الأولى، ومن الدرجة الظاهرية

الثانية، ونموذج الحركة لانتشار الجسيمات. تم حساب ومناقشة المعلمات الحركية، وثوابت المعدل، وقدرات امتزاز التوازن، ومعامل التحديد ذي الصلة لكل نموذج حركي. وقد بينت نتائج الدراسة أن عملية الامتزاز تتوافق مع نموذج فريوندليش، ووجد أن عملية الامتصاص كانت مجدية وتلقائية وممتصة للحرارة، كما تبين أن امتزاز النحاس يمكن وصفه بمعادلة الدرجة الثانية الظاهرية. كما نتبين أن آلية عملية امتزاز النحاس على الكربون المنشط المخضر من الأكاسيا هي عملية امتزاز كيميائي وفق ما بينته معلمات المبينة بالدراسة. أظهرت نتائج الدراسة أن الكربون المنشط حرارياً والمخضر من الأكاسيا يمكن استخدامه بفاعلية باعتباره مادة مازة طبيعية ومنخفضة التكلفة للإزالة الفعالة لأيونات Cu (II) من المحاليل المائية كبديل للممترات التجارية الحالية.

الكلمات الدالة: النحاس، أكاسيا، الاتزان، الحركة، الديناميكا الحرارية، الامتزاز.

1. Introduction

Industrial waste water effluents mostly contain high quantities of toxic and polluting heavy metals. Small-scale factories produce a large amount of emissions and, in many situations, waste water is dumped directly into the environment without adequate treatment. Cu(II) is one of the harmful metal ions from several sectors found in wastewater discharge and effluent. Cu(II) imbalance can cause headaches, fatigue, insomnia, depression, skin rashes, detachment, learning disabilities, or premenstrual syndrome in the body, and it can even lead to accumulation in the kidneys, brain, skin, pancreas, and heart (Eun-Young *et al.*, 2011). The toxicity of Cu(II) to living organisms is essentially exerted on enzymes, especially enzymes whose activity depends on sulphydryl and amino group because Cu(II) like other heavy metals has a high affinity for ligands containing nitrogen and sulfur donors (Vedhavalli and Srinivasan, 2005). Some separation techniques, such as ion flotation, precipitate flotation, and sorptive flotation, are used for copper removal from an aqueous solution. Precipitation, coagulation, adsorption, ion exchange, and membrane filtration are another widely used treatment involved in reducing the metal load (Onundi *et al.*, 2010). In addition, several new methods have been developed using natural materials, biosorbents, and waste materials to remove metals such as copper from waste water. Studies on wastewater treatment for the removal of heavy metals show that the adsorption is most widely and commonly used (Nasim *et al.*, 2004). Adsorption can remove metals from inorganic effluents using activated carbon. Although it is a costly, granular nature, due to its wide surface area, high adsorption power, and surface reactivity, it is the most common adsorbent and has been used with great success. The other adsorbents include agricultural and industrial waste materials that are found to retain toxic metal from the aqueous solution and potentially cheaper adsorbents like wood charcoal, limestone, corn cobs, barley waste, coconut fiber (Nami *et al.*, 2008).

Among the numerous treatment technologies developed for the removal of copper from the aqueous environment, adsorption is receiving increasing attention in becoming an attractive and promising technology because of its simplicity, cheaper pollution control method, ease of operation and handling, sludge free operation, and regeneration capacity. Detailed information on equilibrium, kinetic and thermodynamic properties are required for the design of adsorbents. The adsorption equilibrium provides fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. An isotherm

equation, whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH, usually describes the sorption equilibrium. Thus, an accurate mathematical description of the equilibrium isotherm is essential for the effective design of adsorption contact processes. Also, the design of a sorption system demands the rate of sorption, So this paper focuses on the isotherms, kinetics, and thermodynamic of its sorptive responses for process applications .

The adsorbent used in the present study, Acacia activated carbon (AAC), demonstrated its sorption capacity for removing copper from aqueous systems (Alshuiref *et al.*, 2017). So, the objectives of this paper are mainly broken down to elucidate (i) the rate-limiting process of sorption and (ii) the mechanisms of copper removal. These objectives will be reached by studying the isotherm, kinetic and thermodynamic adsorption of copper onto Acacia activated carbon (AAC) as adsorbent, at different initial concentrations and temperatures.

2. Materials and Methods

2.1. Chemicals

The solutions of Cu^{+2} were prepared by dissolving accurately weighed amounts of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water. Acacia carbon was collected then dried in an air oven at 120°C for 24 hrs then grounded and sieved to obtain desired size fraction using a conventional sieve-shaker (WiseVen) oven as mentioned by Alshuiref *et al.* (2017).

2.2. Adsorption Experiments (Batch system)

A stock solution of 1000 mg/L of Cu (II) was prepared by dissolving 3.9319 g of ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 1000 mL of deionized water in a volumetric flask. It was dissolved by shaking and the volume was made up to the mark. adsorption experiments were carried out by adding AAC to the conical flask in various amounts containing a known concentration of Cu(II) solutions. These solutions are filtered by using (FILTER-LAB) paper Cod. PN1248110 then adding 5 mL of ammonia to measuring the concentrations of residual Cu(II) using spectrophotometer equipment (JENWAY 7305 Spectrophotometer) at selected wavelength $\lambda_{\text{max}} = 615 \text{ nm}$. The optimum parameters of the adsorption process were studied previously and mentioned by Alshuiref *et al.* (2017) as follows: (adsorbent dose 0.5 g/100 mL, agitation speed 300 rpm, pH 6, particle size 0.375 mm, and contact time 120 min.) at room temperature. The isotherms, kinetics, and thermodynamic studies in this study will be done at 298, 308, 318, and 338 K with initial concentrations (100, 300, 500, 700, and 800 mg/L).

2.3. Adsorption Isotherms

The equilibrium relationship between the adsorbate concentration in the solution (Cu^{+2}) and that on the adsorbent surface (AAC) at a given condition is described by an adsorption isotherm. A variety of isotherms have been developed to characterize relationships with equilibrium. Langmuir, Freundlich, Temkin, and Dubinin-Zaverina-Radushkevich (D-Z-R) models were used to define the equilibrium details in the present study.

2.3.1. The Langmuir Isotherm Model

The Langmuir isotherm model (Langmuir, 1918) was used to describe observed sorption phenomena and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. The widely used Langmuir isotherm, (Langmuir, 1918) has found a successful application in many real sorption processes, (Onar *et al.*, 1996; Ho & McKay, 1999; and Özacar, 2003) and is expressed as;

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad \dots\dots (1)$$

An alternative linear form of this model is:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \quad \dots\dots (2)$$

where C_e is the equilibrium concentration of Cu(II) in (mg/L), q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), q_m is the maximum adsorption capacity (mg/g), and K_a is an equilibrium constant (L/mg) related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate. The constants values of q_m and K_a can be determined from the linear plot of C_e/q_e versus C_e . The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process. The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) that can be defined by the following relationship (Anirudhan & Radhakrishnan, 2008; and Das *et al.*, 2014);

$$R_L = \frac{1}{1 + K_a C_o} \quad \dots\dots (3)$$

where C_o is the initial concentration (mg/L) and K_L is the Langmuir equilibrium constant (L/mg). The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) or unfavorable ($R_L > 1$). It can be explained apparently that when $K_L > 0$, sorption system is favorable (Chen *et al.*, 2008).

2.3.2. The Freundlich Isotherm Model

The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces (Cooney, 1999). The Freundlich model is given by Freundlich, (1906) as:

$$q_e = K_F C_e^{1/n} \quad \dots\dots (4)$$

An alternative linear form of this model is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots\dots (5)$$

where K_F is the Freundlich constant related to sorption capacity in (mg/g).(L/g)^{1/n} and n is related to the adsorption intensity of the adsorbent. Where, K_F and $1/n$ can be determined from the linear plot of $\ln(q_e)$ versus $\ln(C_e)$.

2.3.3. The Temkin Isotherm Model

Unlike the Langmuir and Freundlich models, the Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage (Chen *et al.*, 2008).

$$q_e = \frac{RT}{b} \ln(AC_e) \quad \dots\dots (6)$$

A linear form of the Temkin model can be expressed as:

$$q_e = B \ln A + B \ln C_e \quad \dots\dots (7)$$

where C_e is concentration of the adsorbate at equilibrium (mg/L), q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), $RT/b=B$ where T is the temperature (K), and R is the ideal gas constant (8.314 J/mol.K) and A and b are constants. A plot of q_e versus $\ln(C_e)$ enables the determination of constants A and B . The constant B is related to the heat of adsorption and A is the equilibrium binding constant (L/min.) corresponding to the maximum binding energy.

2.3.4. The Dubinin–Zaverina-Radushkevich Isotherm Model

The Dubinin– Zaverina-Radushkevich model was chosen to estimate the heterogeneity of the surface energies. The Dubinin–Zaverina-Radushkevich equation first present by Dubinin *et al.* (1947) has as the following form:

$$q_e = q_m e^{-\beta \varepsilon^2} \quad \dots\dots (8)$$

A linear form of Dubinin– Zaverina-Radushkevich model is:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad \dots\dots (9)$$

where q_m is the Dubinin– Zaverina-Radushkevich monolayer capacity (mg/g), β is a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = \frac{RT}{M} \ln\left(1 + \frac{1}{C_e}\right) \quad \dots\dots (10)$$

where q_m is the theoretical saturation capacity (mol/g), b is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2), and ε is the Polanyi potential, C_e is the equilibrium concentration of adsorbate in solution (mol/L), R (8.314 J/mol.K) is the gas constant, and T (K) is the absolute temperature. The D-Z-R constants q_m and b were calculated from the linear plots of $\ln(q_e)$ versus ε^2 and are given in Table (1). The constant b gives an idea about the mean free energy E_{D-Z-R} (kJ/mol) of adsorption per molecule of the adsorbate (apparent adsorption energy) when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship (Kundu and Gupta, 2006);

$$E_{D-Z-R} = \frac{1}{\sqrt{2\beta}} \quad \dots\dots (11)$$

The apparent adsorption energy is useful for estimating the type of adsorption, if this value is below 8 kJ/mol the adsorption type can be explained by physical adsorption, between 8 and 16 kJ/mol the adsorption type can be explained by ion exchange, and over 16 kJ/mol the adsorption type can be explained by a stronger chemical adsorption than ion exchange (Krishna *et al.*, 2000; Lin and Juang, 2002; Wang *et al.*, 2004; and Mobasherpour *et al.*, 2011).

2.4. Adsorption Kinetics Modeling

To analyze the rate of adsorption and possible adsorption mechanism of copper onto AAS, the simple first order, Lagergren first-order (Lagergren,1898), pseudo second-order (Ho and

Mckay 2000), intra-particle diffusion (Weber and Morris, 1963), and surface mass transfer models (Mckay *et al.*, 1981) were applied to adsorption data.

2.4.1. The Simple-First-Order Kinetic Model

The sorption kinetic may be described by a simple order model (Hossain *et al.*, 2005; and Eligwe & Okolue, 1994). The following simple first order equation describes the change in bulk concentration;

$$C_t = C_i e^{-k_1 t} \quad \dots\dots (11)$$

That can be rearrangement to obtain a linear form:

$$\ln C_t = -k_1 t + \ln C_i \quad \dots\dots (12)$$

where C_t is the concentration of Cu(II) at time t (mg/L), and k_1 and C_i is the first order rate constant, (1/min), and constant (mg/L) respectively. Value of k_1 at 100 mg/L as initial concentration was calculated from the slope and intercept of the plots of $\ln(C_t)$ versus t . Furthermore, Sparks (1989) and Hossain *et al.* (2005) proposed that the simple kinetic models such as simple first- or second-order rate models are not applicable to the adsorption system with solid surfaces.

2.4.2. The Pseudo First-Order Kinetic Model

The Lagergren first-order rate equation is represented as Eqn. (13);

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad \dots\dots (13)$$

Integration of Eqn. (13) and using the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, yields:

$$\ln \left(\frac{q_e}{q_e - q_t} \right) = k_1 t \quad \dots\dots (14)$$

That can be rearrangement to obtain a linear form:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad \dots\dots (15)$$

where q_e and q_t are the amounts of copper adsorbed (mg/g) at equilibrium and at time t , respectively, and k_1 is the Lagergren rate constant of first-order adsorption (1/min). Values of q_e and k_1 at 100 ppm initial concentration were calculated from the slope and intercept of the plots of $\ln(q_e - q_t)$ versus t .

2.4.3. The Pseudo-Second-Order Kinetic Model

The pseudo second-order kinetic model, which is based on the assumption that chemisorption is the rate-determining step can be expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad \dots\dots (16)$$

Integrating Eqn.(16) and applying the boundary conditions, yields:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad \dots\dots (17)$$

That can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots\dots (18)$$

where k_2 is the rate constant of second-order adsorption (g/mg.min). Values of k_2 and q_e were calculated from the plots of t/q_t versus t . Furthermore, the plot of t/q_t versus t at different

temperatures and constants were presented. The initial adsorption rate, h (mg/g.min) at different temperatures was calculated using Eqn. (19) (Sari *et al.*, 2010).

$$h = k_2 q_e^2 \quad \dots\dots (19)$$

2.4.4. The Intraparticle Diffusion Model

The kinetic results were analyzed by the Weber and Morris intra-particle diffusion model to elucidate the diffusion mechanism. The model is expressed as;

$$q_t = k_d t^{0.5} + c \quad \dots\dots (20)$$

where c is the intercept (mg/g) and k_d is the intra-particle diffusion rate constant (mg/g.min^{0.5}). The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate-controlling step. Generally, the k_d value was higher at the higher concentrations. Intra-particle diffusion is the sole rate limiting step if the regression of q_t versus $t^{0.5}$ is linear and passes through the origin. In fact, the linear plots at each concentration did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect, and further showed that intra-particle diffusion was not the only rate-limiting step (Das *et al.*, 2014).

2.5. Error Analysis

Due to the inherent bias resulting from linearization, error function of non-linear regression basin [coefficient of determination (R^2), relative error (RE), and average relative error (ARE)] were employed in this study to find out the best-fit model to the experimental data, formulas are given as following (Paluri *et al.*, 2020);

Coefficient of Determination (R^2);

$$R^2 = \frac{\sum_{i=1}^N (q_{exp} - \bar{q}_{cal.})^2}{\sum_{i=1}^N (q_{exp} - \bar{q}_{cal.})^2 + \sum_{i=1}^N (q_{exp} - q_{cal.})^2} \quad \dots\dots (21)$$

Relative Error (RE);

$$RE = \left| \frac{q_{exp} - q_{cal.}}{q_{exp}} \right| * 100 \quad \dots\dots (22)$$

Average Relative Error (AER);

$$ARE = \frac{100}{N} \sum_{i=1}^N \left| \frac{q_{exp} - q_{cal.}}{q_{exp}} \right| \quad \dots\dots (23)$$

here, $q_{cal.}$ and $q_{exp.}$ are the calculated and the experimental values of the adsorbate solid concentration in the solid phase (mg/g) respectively, $\bar{q}_{cal.}$ is the mean of the calculated ($q_{cal.}$) values, and N is the number of the data points.

2.6. Thermodynamics of Adsorption

To study the feasibility of the adsorption process, the thermodynamic parameters such as free energy, enthalpy and entropy changes can be estimated from the following equations (Senthilkumar *et al.*, 2011; Das *et al.*, 2014; and Yu *et al.*, 2019);

$$\Delta G^{\circ} = -RT \ln K_C \quad \dots\dots (24)$$

$$K_C = \frac{C_{Ae}}{C_e} \quad \dots\dots (25)$$

$$\ln K_C = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad \dots\dots (26)$$

where C_e is the thermodynamic equilibrium concentration in solution in (mg/L) and C_{Ae} is the equilibrium concentration on the sorbent in (mg/L), and K_C is the equilibrium constant. Thermodynamic parameters of adsorption from solutions provide a great deal of information concerning the type and mechanism of the adsorption process. The free Gibbs energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) thermodynamic parameters have been estimated to evaluate the feasibility of the adsorption process. The Gibbs energy change (ΔG°) indicates the degree of spontaneity of an adsorption process, and a higher negative value reflects a more energetically favorable adsorption (Din *et al.*, 2014). Generally, type of adsorption can be explained as physical adsorption occurs with low heat of adsorption (20–40 kJ/mol). In contrast, in chemical adsorption, the heat of adsorption is high i.e. about 40–400 kJ/mol (Sahmoune, 2018). Moreover, adsorption can be divided into chemical adsorption and physical adsorption, both of which can occur simultaneously in one adsorption process. The adsorption heat for van Edward force, hydrogen bond, ligand exchange, dipole interaction, and chemical bond is 4–10, 2–40, \approx 40, 2–29, and >60 kJ/mol, respectively (Xu *et al.*, 2017).

3. Results and Discussion

3.1. Adsorption Isotherms

The equilibrium relationship between the adsorbate concentration in the solution (Cu^{+2}) and that on the adsorbent surface (AAC) at a given condition is described by an adsorption isotherm. A variety of isotherms have been developed to characterize relationships with equilibrium. Langmuir, Freundlich, Temkin, and Dubinin–Zaverina-Radushkevich (D-Z-R) models were used to define the equilibrium details in the present study. The results are presented in Figure (1) and Table (1) shows the modeled isotherms.

The results presented in Table (1) show that, the Freundlich isotherm gave good fit to the experimental equilibrium adsorption data than the Langmuir, Dubinin–Zaverina-Radushkevich, and Temkin isotherm models for Cu(II) sorption according to the values of R^2 and ARE . It was also seen from Table (1) that the Langmuir maximum adsorption capacities (q_m) are ranged between 55.556 and 79.365 mg/g, and the equilibrium constants K_a are ranged between 0.0251 and 0.0632 L/mg.

The average separation factor (R_L) values are 0.1156, 0.0631, 0.0703, and 0.0518 while temperatures are 298, 308, 318, and 338 K, respectively for initial Cu(II) concentrations 100, 300, 500, 700 and 800 mg/L, respectively. All the R_L values were found to be less than one and greater than zero indicating the favorable sorption of Cu(II) onto AAC.

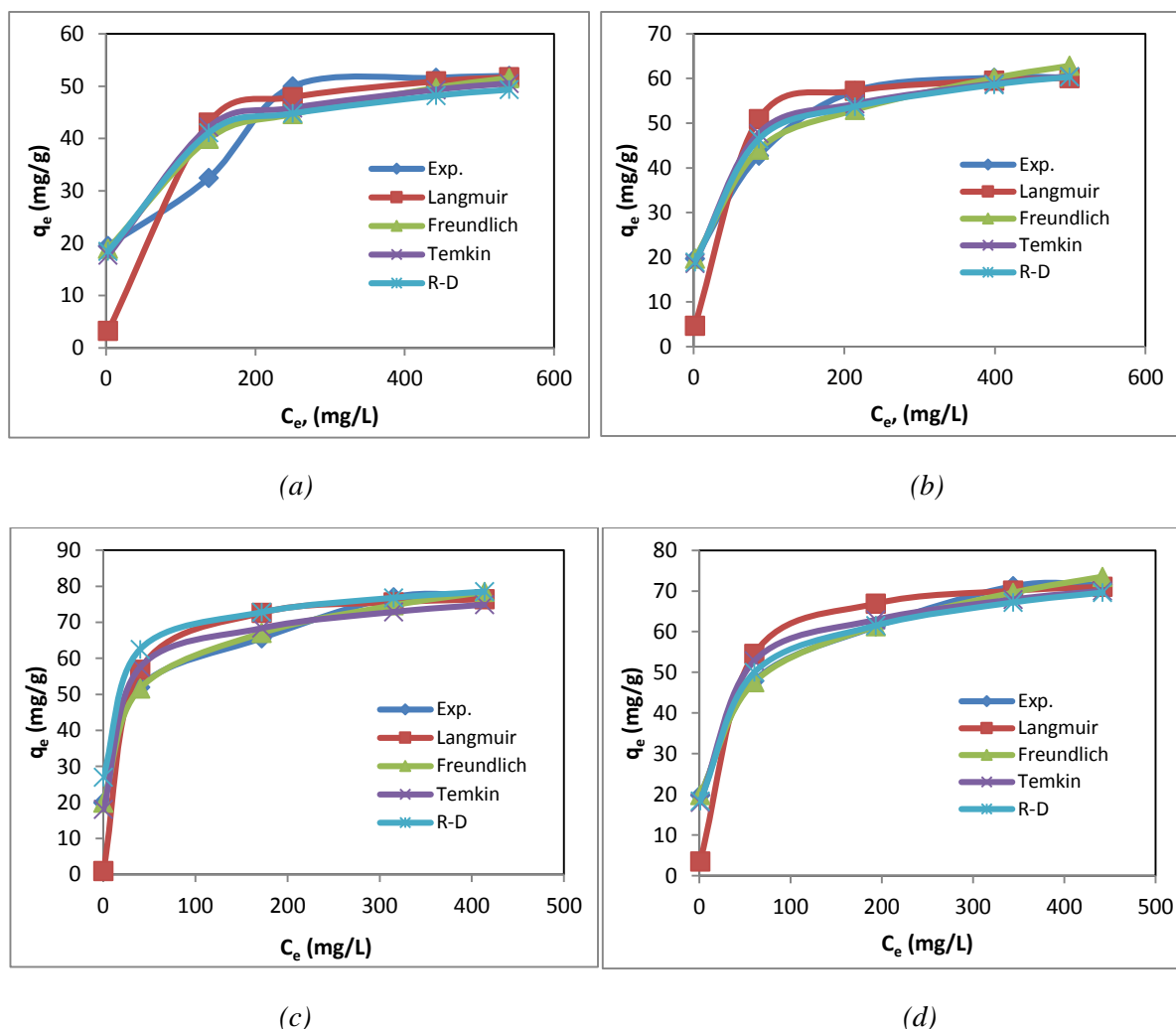


Figure 1. Comparison between the measured and modeled isotherm profiles for the adsorption of Cu(II) ions by AAC. Experimental conditions: (adsorbent dose 0.5 g/100 mL, agitation speed 300 rpm, pH 6, and contact time 120 min.); (a) 298 K, (b) 308 K, (c) 318 K; and (d) 338 K.

The Freundlich constant K_F indicates the sorption capacity of the sorbent, and the values of K_F are ranged between 15.959 and 26.658 mg/g. Furthermore, the values of "n" at equilibrium were ranged between 4.579 and 5.58. The value of "n" between 1 and 10 represents a favorable adsorption (Slejko 1985; and Das *et al.*, 2014). From D-Z-R isotherm, the values of the adsorption energy were found to be ranged between 15.8 and 15.9 kJ/mol. The estimated values of E_{D-Z-R} for the present study were found in the range expected for ion exchange adsorption (Table 1) at temperature ranged from 298-318 K followed by chemical adsorption at 338 K. So, the mechanism for the adsorption of Cu(II) ions by AAC was based on ion exchange followed by complexation with chemical adsorption in nature at high temperature.

Table 1. Adsorption isotherm constants for adsorption of Cu(II) onto AAC

Isotherm	Parameters	Temperature (K)			
		298	308	318	338
Langmuir	q_m (mg/g)	55.556	62.5	74.623	79.365
	K_a (L/mg)	0.0251	0.0508	0.0449	0.0632
	R^2 (-)	0.8201	0.9259	0.9433	0.9514
	ARE (%)	24.325	19.305	21.528	23.626
	R_L (-)	0.1156	0.0631	0.0703	0.0518
Freundlich	K_F (mg/g).(L/mg) ^{1/n}	15.959	17.921	19.434	26.656
	n (-)	5.362	4.95	4.579	5.58
	R^2 (-)	0.9984	0.978	0.9967	0.9961
	ARE (%)	8.199	3.076	1.192	1.499
Temkin	B (mg/g)	6.107	7.288	8.675	7.444
	A (-)	7.278	8.061	7.292	56.811
	R^2 (-)	0.8566	0.9702	0.977	0.9717
	ARE (%)	10.901	4.946	5.671	6.527
D-Z-R	q_m (mg/g)	65.3	82.2	9.84	96
	β (mol ² /kJ ²)	0.002	0.002	0.002	0.00198
	E_{D-R} (kJ/mol)	15.8	15.8	15.8	22.4
	R^2 (-)	0.864	0.977	0.9891	0.973
	ARE (%)	10.766	4.321	4.0912	13.712

The effectiveness of AAC as adsorbent for copper adsorption was also compared with other reported activated carbons obtained from various plants, agricultural and wood based materials. The maximum adsorption capacity obtained in this study is comparable with other adsorbents as shown in Table (2). It is clear that AAC has a good adsorption capacity compared to other adsorbents.

Table 2. Results for adsorption of Cu(II) by activated carbons obtained from various plants, agricultural and wood based materials.

Source of AC	pH	Uptake (mg/g)	References
Apricote stone	6.5	22.85	Kobyia <i>et al.</i> (2005)
Cassava peel	6	52	Moreno-Pirajan <i>et al.</i> (2010)
Ceiba pentandra hulls	6	20.78	Madhava Raoa <i>et al.</i> (2006)
Date stones	6	31.25	Bouhamed <i>et al.</i> (2012)
Grapeseed	5	48.78	Özçimen D. and Ersoy-Meriçboyu (2009)
Olive Waste Cakes	5	106.38	Ibrahim <i>et al.</i> (2016)
Palm shell	5	22	Issabayeva & Aroua (2011)
Pecan shells	4.8	31.7	Bansode <i>et al.</i> (2003)
Phaseolus aureus hulls	7	20	Rao <i>et al.</i> (2009)
Rubber wood sawdust	6	52	Moreno-Pirajan & Giraldo (2010)
Soybean hulls	5	39.37	Johns <i>et al.</i> (1998)
Acacia	6	55.556-79.365	This study

3.3. Adsorption Kinetics Modeling

Based on kinetic data, various models have been suggested which throw light on the mechanisms of sorption and potential rate controlling steps. The models applied to examine the dynamics of the sorption process include simple-first-order, Lagergren's pseudo-first-order, Ho's pseudo-second-order, and the intra-particle surface diffusion model by Weber and Morris were shown in Figure (2) and the calculated parameters of each one are presented in Table (3).

A comparison of the results with the coefficient of determination is shown in Table (4). The pseudo-second-order kinetic model obtained for Cu²⁺ sorption showed better correlation of result than the simple-first order, pseudo-first-order, and Intra-particle diffusion models. The coefficient of determination for the second-order kinetic model obtained at 100 ppm concentrations at different temperatures were high.

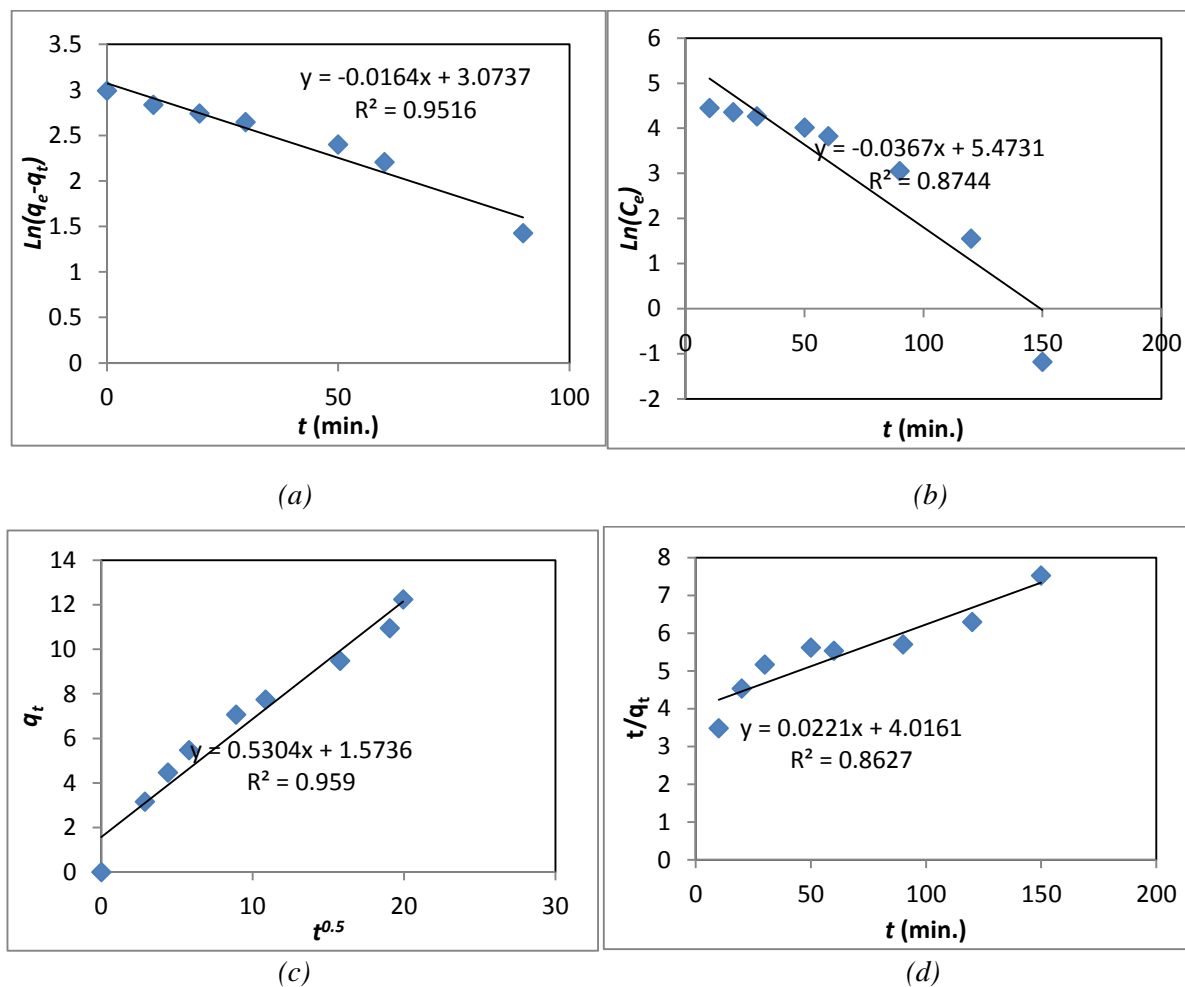


Figure 2. Linear fit Kinetic plots for adsorption of Cu(II) onto AAC with experimental data. (Experimental conditions: initial concentration 100 mg/L, adsorbent dose 0.5 g/100 mL, agitation speed 300 rpm, pH 6, and temperature 298 K).
a) Simple 1st order model, b) Pseudo 1st order model, c) Pseudo 2nd order, and d) Intraparticle diffusion model

Table 3. Kinetic parameters for adsorption of Cu(II) onto AAC

Kinetic model	Parameters	Value
Simple first order (Model 1)	k_1 (1/min)	-0.0367
	C_i (mg/L)	238.197
	R^2 (-)	0.874
Pseudo-first order (Model 2)	k_1 (1/min)	0.016
	q_e (mg/g)	21.622
	R^2 (-)	0.952
Pseudo-second order (Model 3)	k_2 (g/mg.min.)	0.000122
	q_e (mg/g)	45.249
	R^2 (-)	0.863
Intra-particle diffusion (Model 4)	k_d (mg/g.min ^{0.5})	0.5304
	c (-)	1.5736
	R^2 (-)	0.959

It is clear from Figure (3) that the pseudo second-order kinetic model showed excellent confirmation with experimental data in comparison to the other kinetic models, due to the calculated q_t values agree with the experimental data in the case of pseudo second-order kinetic model with low ARE (=7.047%) and high coefficient of determination ($R^2= 0.992$) as shown in Table (4).

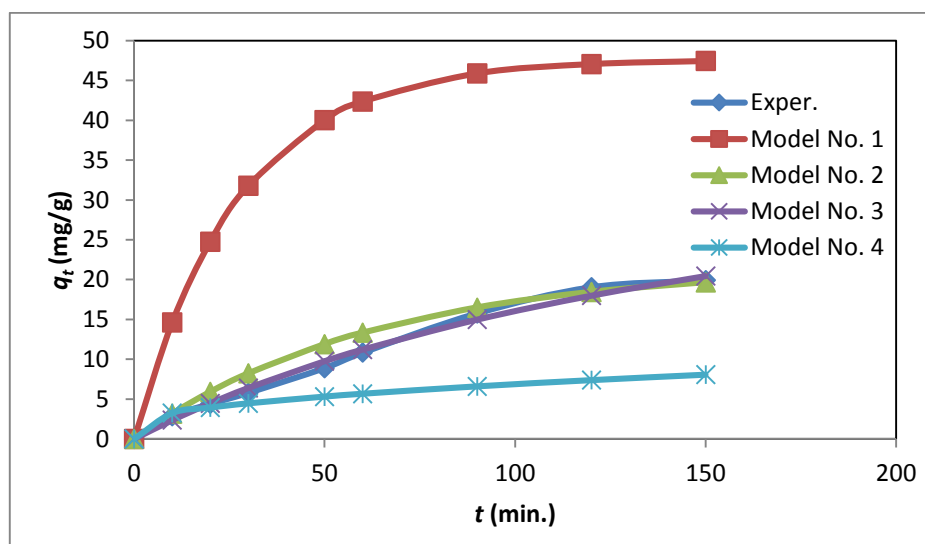


Figure 3. A comparison of experimental Cu(II) adsorption data with the applied kinetic models ($C_o = 100$ mg/L; adsorbent dose 0.5 g/100 mL; agitation speed 300 rpm; pH= 6; and temperature 298 K).

Table 4. A comparison of experimental Cu(II) adsorption data with the applied kinetic models ($C_o = 100$ mg/L; adsorbent dose 0.5 g/100 mL; agitation speed 300 rpm; pH= 6; and temperature 298 K).

Experimental data		Simple-first-order (Model 1)		Pseudo-first order (Model 2)		Pseudo-second order (Model 3)		Intra-particle Diffusion (Model4)	
Time (min.)	$q_{texp.}$ (mg/g)	$q_{texp.}$ (mg/g)	RE (%)	$q_{texp.}$ (mg/g)	RE (%)	$q_{texp.}$ (mg/g)	RE (%)	$q_{texp.}$ (mg/g)	RE (%)
0	0	0		0		0		0	
10	2.870	14.634	409.941	3.197	11.398	2.360	17.761	3.251	13.278
20	4.410	24.773	461.764	5.921	34.269	4.486	1.731	3.946	10.528
30	5.803	31.798	447.978	8.243	42.047	6.411	10.492	4.479	22.817
50	8.903	40.036	349.674	11.906	33.732	9.764	9.663	5.324	40.200
60	10.842	42.371	290.804	13.343	23.066	11.232	3.592	5.682	47.593
90	15.773	45.888	190.929	16.499	4.604	14.987	4.980	6.605	58.121
120	19.051	47.057	147.003	18.452	3.146	17.996	5.538	7.384	61.242
150	19.938	47.446	137.962	19.660	1.395	20.461	2.620	8.070	59.527
ARE (%)			304.507		19.207		7.047		39.163
R^2			0.802		0.946		0.992		0.664

It is also observed from Table (5) that the values of the rate constant k_2 increase with increasing initial Cu(II) concentrations. This is due to the lower competition for the surface active sites at lower concentration, but at higher concentration the competition for the surface active sites will be high and consequently, higher sorption rates are obtained.

Table 5. Pseudo second order parameters calculated at different initial concentrations

Parameters	C_o (mg/L)	100	300	500
q_e (mg/g)		45.249	43.668	34.483
K_2 (g/mg.min.)		0.000121613	0.000467389	0.000848
R^2 (-)		0.863	0.994	0.987

It is also evident from Table (6) that rate constant, k_2 increased as the temperature increased indicating the endothermic nature of adsorption of copper ion onto AAC. Again as evident from Table (6), the initial adsorption rate (h), increased with increase in temperature suggesting that adsorption of copper ion onto AAC was favorable at higher temperatures.

Table 6. Pseudo second order parameters calculated at different temperatures

T (K)	k_2 (g/mg.min)	q_e (mg/g)	H (mg/g.min)
298	0.000122	45.24887	0.2489
308	0.000547	46.439	1.1797
318	0.000867	47.674	1.9712
338	0.001673	48.295	3.9021

On comparing the fitting of the applied kinetic models it can be concluded that, the kinetic profile can be best modeled by pseudo-second-order model indicative of a chemical effect is involved in the adsorption (Ayooob *et al.*, 2008). Therefore, it could be concluded that the rate-limiting step of Cu(II) adsorption onto AAC may be ion exchange followed by chemisorption at high temperature. Some authors consider ion exchange process as a chemisorption mechanism (Sahmoune, 2018).

It was suggested that the value of energy of activation value (E_a), obtained from Arrhenius equation [Eqn. (27)] could also be a useful kinetic parameter in assessing rate-limiting steps (Ayooob *et al.*, 2008). Some of the assigned values of E_a (kJ/mol) include 8-25 to physical adsorption, less than 21 to aqueous diffusion, 20-40 to pore diffusion and greater than 84 to ion exchange (Sahmoune, 2018):

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad \dots\dots (27)$$

where k_2 is the rate constant, A is the Arrhenius constant, E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/(mol.K)), and T is the temperature (K). By plotting $\ln(k_2)$ versus $1/T$, E_a was obtained from the slope of the linear plot (Figure 4). The value was found to be 51.286 kJ/mol. The positive value of E_a suggest that increase in temperature favors the

adsorption. In this study, the calculated value of E_a is in high value, suggesting that the intra-particle and pore diffusion is part of the adsorption step, but not the only speed control. Other mechanisms such as complex or ion exchange can also control the rate of adsorption as mentioned by Labidi *et al.* (2016).

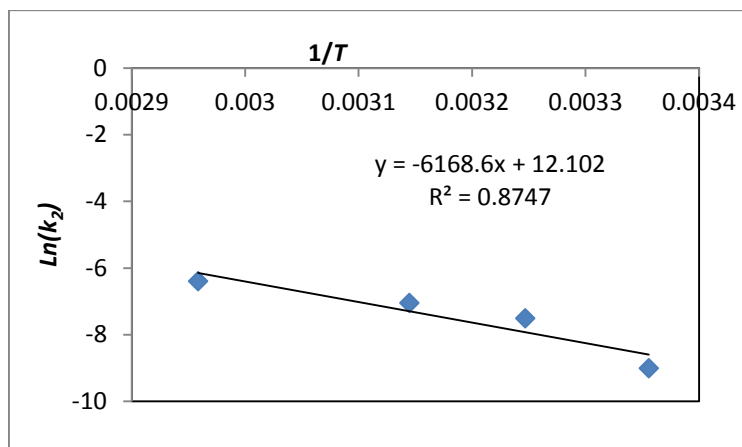


Figure 4. Arrhenius plot for adsorption of Cu(II) onto AAC

3.4. Thermodynamics of Adsorption

The Gibbs free energy (ΔG^0) for the adsorption of Cu(II) onto AAC at all temperatures was obtained from Eqn. (24) and presented in Table (7). The values of (ΔH^0) and (ΔS^0) were calculated from the slope and intercept of the plot $\ln(K_c)$ against $1/T$ as shown in Figure (5) according to Eqns. (25 and 26) and are listed in Table (7).

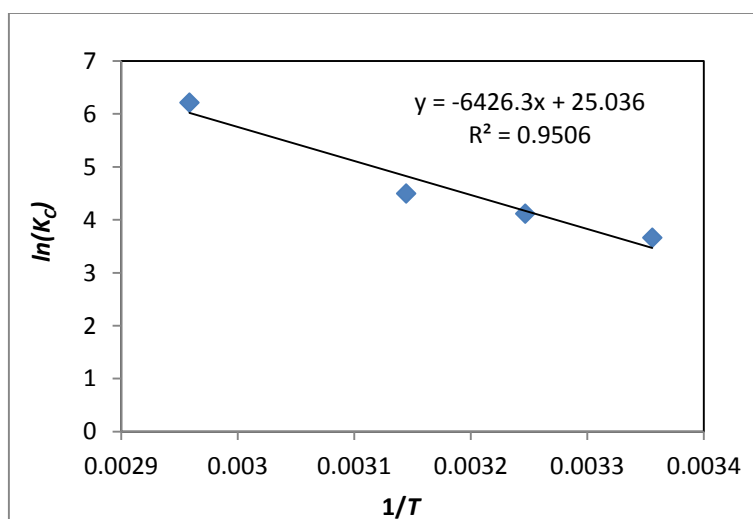


Figure 5. Plot of $\ln(K_c)$ vs. $1/T$ for estimation of thermodynamic parameters for the adsorption of Cu(II) onto AAC.

Table 7. Thermodynamic parameters for the adsorption of Cu²⁺ onto AAC

<i>T</i> (K)	Thermodynamic Properties		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
298	-9.077		
308	-10.548		
318	-11.894	53.428	0.2081
338	-17.458		

The negative values of ΔG° show the thermodynamic feasibility and spontaneity of adsorption and also the ΔG° value decreased when the temperature increased from 298 to 338 K, (Table 7) suggesting more efficient adsorption at higher temperatures. At higher temperature, ions are readily desolvated and therefore their adsorption becomes more favorable.

The positive values of ΔH° suggest the possibility of a strong binding between Cu(II) and AAC and confirm endothermic process. The positive value of ΔS° reflect good affinity of the adsorbent for the metal ions, indicating an increase in sorbate concentration in the solid-liquid interface (Mustapha *et al.*, 2019). That indicates that an increasing randomness occurs at the solid-solution interface during the adsorption of Cu(II) ions onto AAC, since adsorbed ions led to decreasing number of water molecules surrounding adsorbate cations and thus the degree of freedom of the water molecules increases (Anirudhan & Suchithra, 2010; and Yu *et al.*, 2019). Moreover it was found that $\Delta H^{\circ} < T \cdot \Delta S^{\circ}$, indicating that the influence of entropy is more remarkable than enthalpy of the activation in this work.

The magnitude of ΔH° is a useful mean for evaluating the type of adsorption process. In this study, the ΔH value was 53.428 kJ/mol, indicating the adsorption by indicating the adsorption ligand exchange and chemical bond. Therefore, the adsorption of Cu²⁺ onto AAC is chemical adsorption.

4. Conclusion

It would be concluded on the surface coverage that the activated carbon prepared from Acacia (AAC) has considerable potential for removal of Cu²⁺ ions from aqueous solution over a wide range of concentrations. The value of the maximum adsorption capacity was ranged between 55.556 and 79.365 mg/g for initial concentrations in the range 100-800 mg/L, these values are comparable with the values for activated carbon reported in earlier studies. Adsorption isotherms of these Cu(II) ions on the AAC were studied and modeled using four isotherm models. The classification of the models according to the simulation of the adsorption isotherms is; Freundlich > Temkin > D-Z-R > Langmuir. An excellent prediction in the studied concentration can be obtained by the Freundlich isotherm with small values of ARE% and high values of R². Kinetics adsorption of Cu(II) ions on the AAC were studied and modeled using four kinetic models. The classification of the kinetic models according to the

simulation of the adsorption is; Pseudo-second-order > Pseudo-first-order > Intra-particle diffusion > Simple-first-order. The rate of adsorption was found to obey pseudo-second-order kinetics with small values of $ARE\%$ and high values of R^2 . The second-order kinetic model was successfully applied to the experimental data, confirming that the adsorption mechanism was controlled by chemical adsorption. Also, this mechanism is inferred from the D-Z-R isotherm model. The calculated thermodynamic parameters showed the endothermic, spontaneous nature, and predominantly chemical adsorption of Cu(II) onto AAC. The present findings suggest that AAC may be used as an inexpensive and effective adsorbent for the removal of copper ions from aqueous solutions without any treatment or any other modification.

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