

Research Article

Kinetic and Isotherm Studies of the Adsorption Phenacetin onto Two Copper Porous Coordination Compounds: Nonlinear Regression Analysis

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Two coordination compounds, copper (II) fumarate (CuFum) and copper (II) tartrate (CuTart), synthesized from copper (II) with fumaric acid and tartaric acid as ligands and using the slow evaporation method have been applied to study the adsorption of phenacetin in aqueous solution. These compounds were characterized by elemental analysis, IR-FT spectroscopy, and X-ray powder diffraction. The melting points of the synthesized coordination compounds were found to be above 350°C. The influence of parameters such as the initial pH, the contact time, and the initial concentration on the adsorption of phenacetin in an aqueous solution has been studied. The studies showed that adsorption equilibrium was reached after 80 minutes for both coordination compounds; the adsorption capacity increased with increasing phenacetin concentration, and the maximum adsorption capacity was obtained in the acidic medium at pH 4. The adsorbed amount of phenacetin on copper (II) fumarate (CuFum) was 25.158 mg/g while that on copper (II) tartrate (CuTart) was 25.906 mg/g. Nonlinear regression analysis showed the best fit for the Freundlich model isotherm for CuTart with R^2 of 0.963 and a Chi-square test (χ^2) of 0.529 while for the CuFum material, it is the Redlich-Peterson model with R^2 of 0.975 and Chi-square test (χ^2) of 0.263. The kinetic study shows that the pseudo-second-order model better describes the adsorption of the two materials. The results show that physisorption and chemisorption participate in the adsorption of phenacetin and that these materials can be used for the elimination of phenacetin in solution.

1. Introduction

Phenacetin, also known by the designations pethoxyacetanilide, aceto-4-phenetidine acetophenetidin, N-acetyl-p-phenetidine, and acetophenetidine, is a non-opioid antipyretic and analgesic. It can be isolated from *Bursera grandifolia*, a herbal remedy with antipyretic properties [1]. The antipyretic effect was observed by its action on the brain via a

decrease in the temperature set point [2]. Phenacetin is also used principally as an analgesic for the treatment of fever and related complications [1, 3]. The analgesic effects were observed through its activities on the sensory tracts of the spinal cord. However, the long-term and chronic consumption of phenacetin led to several toxicological complications ranging from nephrotoxicity to carcinogenicity [4]. The carcinogenicity was observed in the urinary tract and renal pelvis [5]. As

a result of these severe complications, phenacetin and drugs containing phenacetin were withdrawn from the market by the order of the U.S. Food and Drug Administration in 1983 [6].

Due to its low cost, phenacetin is still being used for research into the physical and refractive properties of crystals [7]. Conventional methods are being used to remove pharmaceutical compounds from wastewater; some examples of which are chlorination, oxidation, biological treatment, electrochemical treatment, and adsorption. However, the adsorption method has many advantages over the others, such as easy operation, high efficiency, and no risk of highly toxic sub-products [8]. The most used adsorbents for the removal of pharmaceutical compounds from aqueous solution are activated carbons [9–11] clay minerals [12], polymeric resins [13], and other adsorbents, such as molecular polymers [14], mesoporous materials [15], and metal-organic frameworks [16]. Despite all these, it is still of interest to study modified adsorbents or new adsorbents that may be more efficient at removing pharmaceutical compounds from water than conventional ones.

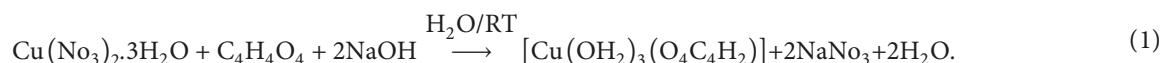
Metal-organic frameworks (MOFs) are a new class of adsorbent materials, with high porosity and high specific area that is formed by metal ions linked to organic ligand bridges, to generate coordination compounds that extend into space in all dimensions. These materials allow a more flexible design of chemical functionality and easy modification, which makes them more promising materials for the adsorption of pharmaceutical compounds. Among the MOFs, a porous Cu-based MOF based on a pentacarboxylate ligand 2,5-bis(3,5-dicarboxyphenyl)-benzoic acid (H_5L), namely, $[(CH_3)_2NH_2]\{[Cu_2(L)\cdot(H_2O)_2]\cdot x \text{ solvent}\}_n$, has been used as a sorbent to remove diclofenac sodium and chlorpromazine hydrochloride from the aqueous solution [17]. These compounds exhibit excellent gas adsorption capacities taking advantage of large permanent porosity and excellent diclofenac adsorption in an aqueous solution.

In this work, we used copper (II) fumarate and copper (II) tartrate as novel adsorbents. These adsorbents have never been used for the adsorption of any pollutants. Hence, this work aimed to evaluate the adsorption properties of these complexes for the removal of phenacetin from an aqueous solution. Isotherms studies were carried out, and the experimental data were analyzed using the two-parameter non-linear regression kinetics, and two and three-parameter non-linear isotherm models.

2. Materials and Methods

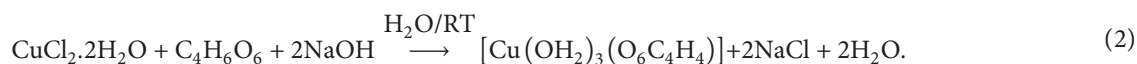
2.1. Phenacetin. Phenacetin with a purity of 98% was purchased from Aldrich. The stock solution was prepared by dissolving 250 mg of phenacetin in 100 mL of hot distilled water (75°C). Working solutions of concentration varying between 20–50 mg/L were freshly prepared by diluting the stock solution. NaOH (0.10 M) and HCl (0.10 M) were used to adjust the pH value of the phenacetin solutions. Distilled water was used throughout this study.

2.2. Adsorbents. Copper (II) fumarate (CuFum) was synthesized hydrothermally as follows: In a 50 mL round-bottomed flask containing about 20 mL of distilled water, were introduced fumaric acid, $C_4H_4O_4$ (196.07 mg; 1.23 mmol) and sodium hydroxide, NaOH (80 mg; 2 mmol) which dissolved instantly under magnetic stirring. To the colorless solution obtained was added copper (II) nitrate trihydrate, $Cu(NO_3)_2\cdot 3H_2O$ (384.7 mg, 1.23 mmol). The resulting solution was kept under continuous stirring for 24 hours. At the end of this time, a blue precipitate was formed which was collected by filtration. Subsequently, the blue powder obtained (396.4 mg) was washed with distilled water and dried at room temperature. The yield from this synthesis was 60%. The balanced equation of this reaction is as follows:



Copper (II) tartrate (CuTart) was prepared according to the method described by Al-Dajani et al. [18] as follows: In a round-bottomed flask containing about 20 mL of distilled water, tartaric acid was introduced, $C_4H_6O_6$ (150 mg, 1 mmol) and sodium hydroxide, NaOH (80 mg, 2 mmol) which gradually dissolved under magnetic stirring. To the colorless solution obtained was added copper (II) chloride

dihydrate, $CuCl_2\cdot 2H_2O$ (170.5 mg, 1 mmol). A pale green precipitate was gradually formed upon magnetic stirring for over 24 hours. The mixture was filtered and the residue dried at room temperature. A green powder (174 mg) was obtained, with a yield of 44%. The balanced equation for this reaction is as follows:



2.3. Samples Characterization. Elemental analysis was performed using a Euro Vector CHNS-O element analyzer. FT-IR spectra were recorded using a Perkin-Elmer FT-IR 100

spectrophotometer. The melting point of the compound was obtained using an SMP3 Stuart Scientific melting point apparatus, while the UV-vis spectrophotometer model

GENESYS 10S was employed to record the electronic spectra of the investigated compounds. Powder X-rays diffraction was performed using STOE Stadi-p X-ray powder diffractometer with Cu K α 1 radiation ($\lambda = 1.54056 \text{ \AA}$; Ge monochromator; flat samples) in transmission geometry.

2.4. Adsorption. Adsorption experiments were carried out by mechanical agitation at room temperature. For each run, 25 mL of phenacetin solution of a known initial concentration between 20 and 50 mg/L was treated with 35 mg of the two compounds. After agitation, the solution was filtered, and the filtrate was analyzed to obtain the concentration of the residual phenacetin by using the UV/Vis spectrophotometer (GENESYS 10S). Similar measurements were carried out by varying the pH of the solution and contact time. The amount (Q_t) of phenacetin adsorbed was calculated using the following expression:

$$Q_t = \frac{(C_o - C_t)V}{m}, \quad (3)$$

where C_o is the initial concentration of the phenacetin, C_t is the concentration at time t , V is the volume of the solution, and Q_t is the quantity of phenacetin adsorbed at time t while m is the mass of the adsorbent.

2.4.1. Effect of Initial pH. To determine the effect of pH, the adsorption of phenacetin by each adsorbent was investigated over a pH range of 2 to 10 at ambient temperature. For each adsorbent, 35 mg was treated with 25 mL of an aqueous solution of 40 mg/L of phenacetin. The initial pH of the solution was adjusted by adding HCl or NaOH solution at a concentration of 0.01 mol/L.

2.4.2. Effect of Contact Time. To determine the effect of agitation time on the adsorption process, 35 mg of adsorbent was agitated in a 25 mL solution of phenacetin with an initial concentration of 40 mg/L for different contact times varying between 5 and 120 minutes. After each contact time t , the solution was rapidly filtered and the residual concentration was determined by spectrophotometry. The amount (Q_e) of phenacetin adsorbed was calculated using equation (4).

2.5. Equilibrium Isotherms. To study the equilibrium of the adsorption of phenacetin onto each adsorbent, data from the equilibrium experiments were analyzed using non-linear equilibrium models of two- to three parameters.

Langmuir isotherm: the Langmuir isotherm is often used for the equilibrium adsorption of solutes from solutions. It is expressed as [19]:

$$Q_e = \frac{Q_m K C_e}{1 + K C_e}, \quad (4)$$

where Q_e is the adsorption capacity at the equilibrium concentration (mg/g); C_e is the equilibrium concentration of adsorbate in solution (mg/L), while Q_m is the maximum

adsorption capacity (mg/g) and K is the Langmuir constant (L/m).

Freundlich isotherm: the Freundlich isotherm is an empirical equation employed to describe multilayer adsorption. This model predicts that the pharmaceutical concentration on the adsorbent will increase with the increase in the adsorbate concentration in the solution. The model equation is given as [20]:

$$Q_e = K_f C_e^{1/n}, \quad (5)$$

where K_f (L/mg) is the Freundlich isotherm constant and $1/n$ is the heterogeneity factor which can vary between 0 and 1.

Elovich isotherm: the Elovich isotherm is an equation employed to describe monolayer adsorption. This model predicts that chemical bonds are formed between adsorbents and adsorbates. The model equation is given as [21]:

$$\frac{Q_e}{Q_m} = K_E C_e \exp\left(-\frac{Q_e}{Q_m}\right). \quad (6)$$

Here, K_E is the Elovich constant.

Temkin isotherm: the Temkin isotherm assumes that the decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. It is expressed by the following equation [22]:

$$Q_e = \frac{RT}{b} \ln(AC_e), \quad (7)$$

where $b = RT/B$ is related to the heat of adsorption (J/mol), R is the gas constant (8.314 J/mol-K), T is the absolute temperature (K), and A is the Temkin equilibrium constant (L/g) corresponding to the maximum binding energy.

Redlich-Peterson isotherm: the Redlich-Peterson is an empirical isotherm that incorporates three parameters. It may be used to represent adsorption equilibrium over a wide concentration range. It combines some elements from both the Langmuir and Freundlich equations, and consequently, it can be employed either in heterogeneous or homogenous systems [23]. It can be described as follow:

$$Q_e = \frac{A_{RP} C_e}{1 + B_{RP} C_e^\beta}, \quad (8)$$

where A_{RP} (L/g) and B_{RP} (L/mg) are Redlich-Peterson isotherm constants, β is an exponent which lies between 0 and 1.

Langmuir-Freundlich isotherm: the Langmuir-Freundlich isotherm includes the knowledge of adsorption on heterogeneous surfaces. It describes the distribution of adsorption energy onto the heterogeneous surface of the adsorbent [24]. It can be described as follow:

$$Q_e = \frac{Q_m K_{LF} C_e^\beta}{1 + K_{LF} C_e^\beta}, \quad (9)$$

where Q_e is the equilibrium adsorbed quantity (mg/g); C_e is the equilibrium adsorbate concentration (mg/L); β is the heterogeneity parameter and it has values between 0 and 1 and K_{LF} is the equilibrium constant of the Langmuir-Freundlich equation (L^β/mg^β) for a heterogeneous solid.

2.6. *Kinetic Models.* Four different kinetic models were considered for this study: pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion.

Pseudo-first-order model: the pseudo-first-order kinetic model describes an adsorption process base on multilayer adsorption. Its equation is generally expressed as follows:

$$Q_t = Q_e [1 - \exp(-K_1)t], \quad (10)$$

where Q_e and Q_t are the adsorption capacities at equilibrium and at time t , respectively (in mg/g) and K_1 is the rate constant for the pseudo-first-order adsorption (L/mg.min)

Pseudo-second-order model: the pseudo-second-order kinetic model was initially proposed as a second order rate equation for the removal of heavy metals from water using natural zeolites and it was based on the strong bond between adsorbent and adsorbate [25].

$$Q_t = \frac{Q_e^2 K_2 t}{1 + Q_e K_2 t}, \quad (11)$$

where K_2 is the rate constant for the pseudo-second-order adsorption (L/mg.min).

Elovich model: the Elovich empirical equation model was firstly for the adsorption of carbon monoxide onto manganese dioxide [26]. However, this equation is now generally known as the Elovich equation and has been extensively applied to chemisorption data. This equation can be expressed mathematically as follows:

$$Q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta}, \quad (12)$$

where α (mg/g.min) represents the initial rate of adsorption and β (mg/g.min) the desorption rate constant.

Intra-particle diffusion model: the intraparticle diffusion model developed by Weber and Morris is presented as follows [19, 20]:

$$Q_t = K_{id}t^{1/2} + C, \quad (13)$$

where C (mg/g) is a constant associated with the thickness of the boundary layer and its higher value corresponds to a greater effect on the limiting boundary layer. K_{id} (mg/g.min^{-1/2}) is the rate constant of the intra-particle diffusion model.

2.7. *Error Functions.* In this study, non-linear regression was applied using the Microsoft Excel Solver function from Excel Microsoft 2013 for fitting the curve. The best fit for experimental data was determined from the coefficient of determination (R^2), residual root mean square error (RMSE), Chi-square test (χ^2), Sum Square of Errors (SSE), and Average Relative Error (ARE). The expressions of the error functions are given as follows:

$$\chi^2 = \sum_{i=1}^N \frac{(Q_{e, \text{exp}} - Q_{e, \text{cal}})^2}{Q_{e, \text{cal}}}, \quad (14)$$

$$\text{RMSE} = \sqrt{\frac{1}{n-2} \sum_{i=1}^N (Q_{e, \text{exp}} - Q_{e, \text{cal}})^2}, \quad (15)$$

$$\text{SCE} = \sum_{i=1}^N (Q_{e, \text{exp}} - Q_{e, \text{cal}})_i^2, \quad (16)$$

$$\text{ARE} = \frac{100}{N} \sum_{i=1}^N \left| \frac{Q_{e, i, \text{cal}} - Q_{e, i, \text{exp}}}{Q_{e, i, \text{exp}}} \right|, \quad (17)$$

$$R^2 = \frac{\sum_{i=1}^N (Q_{e, \text{cal}} - Q_{e, \text{exp}})^2}{\sum_{i=1}^N (Q_{e, \text{cal}} - Q_{e, \text{exp}})^2 + (Q_{e, \text{cal}} - Q_{e, \text{exp}})^2}, \quad (18)$$

where $Q_{e, \text{exp}}$ and $Q_{e, \text{cal}}$ (mg/g) are the equilibrium capacity of adsorption obtained from the experiment and by calculating from the model, respectively, and N is the number of data points.

3. Results and Discussions

3.1. Characterization of Copper (II) Carboxylate

3.1.1. *Copper (II) Fumarate (CuFum).* The synthesized copper (II) fumarate was a blue powder that was found to be insoluble in toluene, distilled water, ethanol, acetone, and acetonitrile. It was soluble in DMSO and its boiling point was as high as 350°C.

(1) *Infrared Spectroscopy.* The IR spectrum of the copper (II) fumarate (Figure 1) shows the presence of organic ligands used in the synthesis through the typical vibrations of carboxylic groups.

In the analysis region, the complex shows a low-intensity peak around 3566.78 cm⁻¹ corresponding to the O-H group, which could indicate that this compound contains water molecules. This frequency is slightly lower than 3600 cm⁻¹, indicating that these water molecules may be linked to the central metal or engaged in interactions with its surroundings. This spectrum also exhibits a broad band with a maximum centered around 2895.62 cm⁻¹; which is characteristic of aliphatic C-H vibrations of elongation. This band, expected around 3000 cm⁻¹ is slightly shifted towards low frequencies. The bands observed at 1395.41 cm⁻¹ and 1533.41 cm⁻¹ could correspond respectively to asymmetric vibration of COO⁻ and symmetric vibration of COO⁻ in the fumarate, with a difference of 138.01 cm⁻¹ which reflects a bridging coordination mode of this grouping [27, 28]. The absence of any band around ≈1710 cm⁻¹ indicates the total deprotonation of all carboxylate groups in the complex [29]. The band at 1214.78 cm⁻¹ can be assigned to the C-O group of the fumarate. The band observed

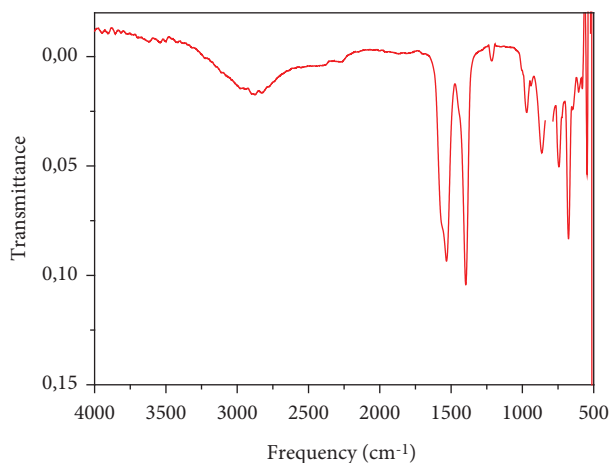


FIGURE 1: Infrared spectrum of copper (II) fumarate.

in the interval $998.97\text{--}989.84\text{ cm}^{-1}$ represents the valence vibrations, that are characteristic of the C=C deformation group. Finally, the absorption bands between 691.92 and 579.38 cm^{-1} are the characteristic frequencies of the Cu-O bond. From the attributions from the IR spectrum, it can be said that the product formed is a copper complex based on the fumarate ligand.

(2) *Elemental Analysis*. The experimental results obtained from the elemental analysis of the synthesized compound and the relative theoretical values are presented in Table 1 below.

The comparison of the percentages of the different elements (C and H) obtained experimentally and theoretically, as well as infrared spectroscopy permitted us to propose the empirical formula $[\text{Cu}(\text{O}_4\text{C}_4\text{H}_2)_2(\text{H}_2\text{O})_4]$ for the compound. The analysis we were able to have was about (C,H,N), but the result shows us that the compound contained only C and H with is in accordance since the reactant used does not contain Nitrogen.

Figure 2 below shows the XRD of the adsorbent copper (II) fumarate obtained between 5 to 80° .

(3) *Powder X-ray Diffraction*. This diffractogram shows sharp Bragg peaks of good intensity indicating that the material has high crystallinity.

From the empirical formula proposed by elemental analysis, and the functional group shown by Infrared spectroscopy, the following structure was proposed for the compound.

3.1.2. *Copper(II) Tartrate (CuTart)*. The results of the UV-Vis spectroscopy, IR spectroscopy, and powder XRD of the synthesized copper(II) tartrate are similar to those obtained from the literature [30]. The structure proposed from the analyses is the following:

3.2. Adsorption Study

3.2.1. *Effect of Initial pH*. The effect of initial pH on the adsorption of phenacetin by the two porous coordination compounds was studied by varying the initial pH of the

TABLE 1: Composition of analyzed elements for $[\text{Cu}(\text{O}_4\text{C}_4\text{H}_2)_2(\text{H}_2\text{O})_4]$.

	% C	% H
Experimental values	25.623	4.331
Theoretical values	26.27	3.86

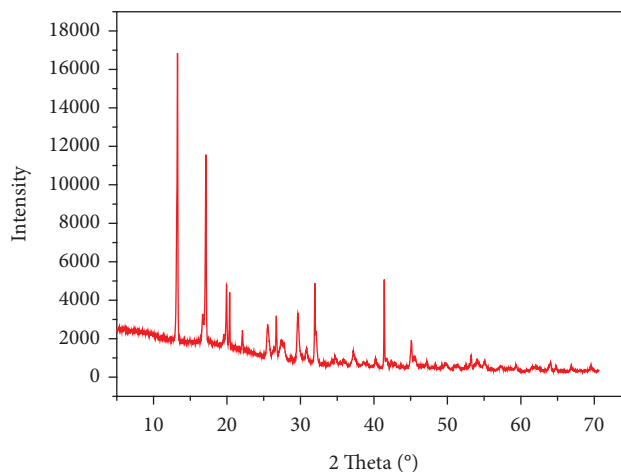


FIGURE 2: Powder X-rays diffraction of copper (II) fumarate.

phenacetin solution. The result is shown in Figure 3. According to this figure, the removal of phenacetin from an aqueous solution is highly dependent on the pH of the solution. Figure 4 shows that the adsorption is maximum at pH 4 with 17.928 mg/g and 19.631 mg/g adsorbed for copper (II) fumarate and copper (II) tartrate, respectively. The decrease in the amount of phenacetin adsorbed at pH greater than 4 can be explained by repulsive electrostatic interactions between an adsorbent and the adsorbate. The amount of phenacetin adsorbed by copper (II) tartrate is greater than that for copper (II) fumarate. This could be explained by the presence in copper (II) tartrate of hydroxide groups which are absent in copper (II) fumarate.

3.2.2. *Effect of Contact Time*. The time of agitation is a very significant parameter in the adsorption process because it determines the time necessary to reach equilibrium adsorption. The adsorption of phenacetin from an aqueous solution of an initial concentration of 40 mg/L and pH 4 was carried out on 35 mg of each carboxylate at the rotational speed of 150 rpm . The result obtained for the increasing stirring times is shown in Figure 5 which gives the amount of phenacetin adsorbed (Q_t) as a function of time.

Figure 5 shows that the adsorption takes place in three phases. The first rapid phase occurs during the first 20 minutes and the second phase takes place a little more slowly, stopping at equilibrium which is 80 min for the metal carboxylates. The rapidity of the first phase can be explained by a large number of sites available at the start of the adsorption process. This availability favors their occupation by the molecules of phenacetin. The same trend was observed by Gadipelly et al. [16] during the adsorption of ciprofloxacin onto MOF-5 (zinc (II) benzene dicarboxylate). As the

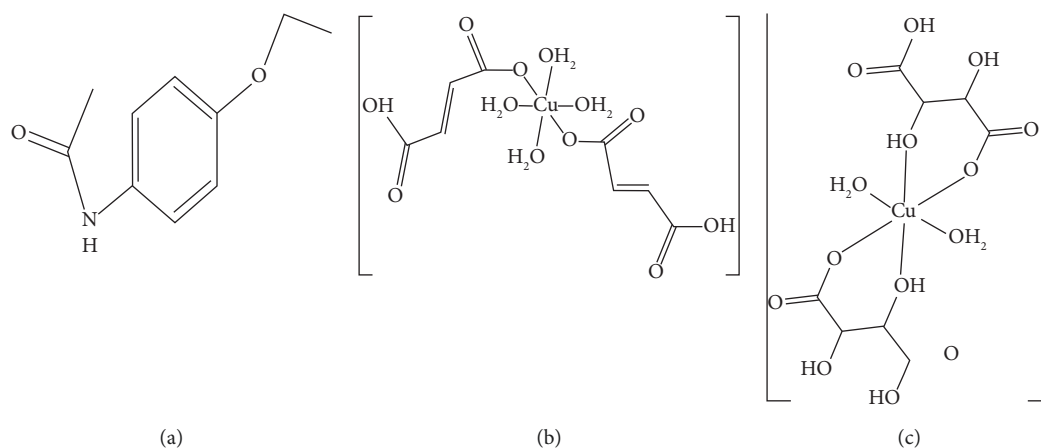


FIGURE 3: Structure of phenacetin (a), copper (II) fumarate (CuFum) (b) and copper (II) tartrate (CuTart) (c).

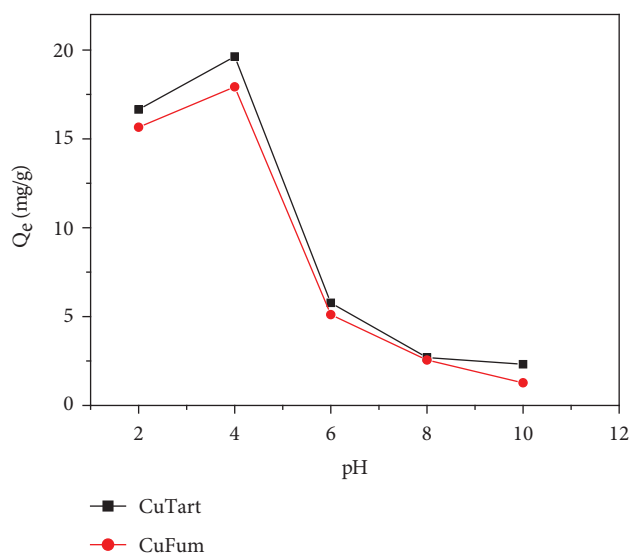


FIGURE 4: The effect of pH on the adsorption of phenacetin onto CuTart and CuFum.

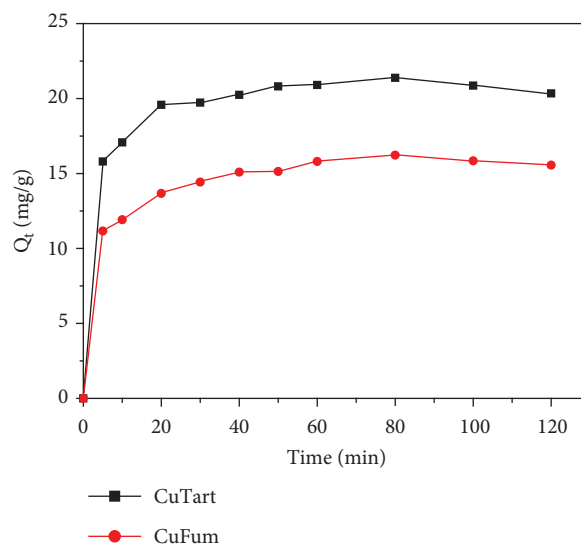


FIGURE 5: Effect of contact time on the adsorption of phenacetin onto CuTart and CuFum.

adsorption continues, the number of available sites decreases and the adsorbent becomes saturated. The amount of phenacetin adsorbed during this phase can be attributed to the π - π interactions between the organic compounds and adsorbents. The adsorption capacity of copper (II) tartrate is 21.381 mg/g while that of copper (II) fumarate is 16.225 mg/g.

3.2.3. Effect of Initial Concentration. The effect of initial concentration on the adsorption of phenacetin was investigated and the results are shown in Figure 6 below.

The increasing adsorption capacities of the porous coordination compounds with the increase in the concentration of phenacetin may be due to π - π interactions between the organic compounds and adsorbents. The π - π interactions in most cases are responsible for the mechanism of adsorption of aromatic compounds [31]. This result can also be explained by saying that, increasing the initial concentration of phenacetin leads to an increase in the driving force of mass transfer and hence an increase in the rate at which phenacetin molecules

pass from solution to the particle surface [32]. The quantity of phenacetin adsorption onto all samples of porous coordination compounds did not show a plateau, suggesting that there was no monolayer formation on the surfaces of the adsorbents. The increase in adsorption capacity with an increase in initial concentration indicates that the porous coordination compounds have a high potential for the removal of phenacetin from their solutions.

3.3. Isotherm Study. In general, the adsorption isotherm indicates how the molecules are distributed between the liquid and solid phase when the adsorption processes attain equilibrium. This part aims at finding the models that can accurately describe the data obtained from the experiments of the adsorption of phenacetin onto copper (II) fumarate and copper (II) tartrate. Three models of two-parameter isotherms and two models of three-parameter isotherms were studied. The non-linear plots of these isotherms are given in Figures 7 and 8.

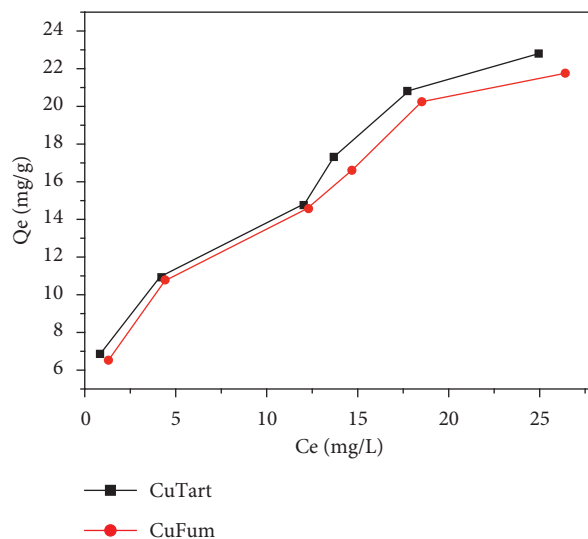


FIGURE 6: Effect of initial concentration on the adsorption of phenacetin onto CuTart and CuFum.

The analysis in Table 2 shows that among the two-parameter isotherms studied, the Freundlich model is the one that best describes the metal carboxylate adsorption phenomenon. This is due to its coefficient of determination which tends toward 1 and the values of the error functions which are lower than those obtained by the other models. The validation of the Freundlich model allows us to say that it is a multilayer adsorption on a heterogeneous surface for the two adsorbents, and the interactions between the adsorbent's surface and the adsorbate play a significant role in the adsorption process [33]. The value of $1/n$ less than 1 in the Freundlich model shows that there is an affinity between the surface of the materials and the adsorbate solution. These values support the hypothesis that the surfaces of the different materials are heterogeneous [33]. The change in adsorption energy ΔQ obtained from the Temkin model is positive regardless of the material, which means that the adsorption process is exothermic.

By still using Table 3, and considering the three-parameter isotherms, it can be deduced that based on the low error values and the high values of the coefficient of determination, the best representation of the experimental adsorption data is given by the Redlich-Peterson model. This implies that the adsorption of the phenacetin by the different materials takes place on heterogeneous surfaces. Its heterogeneity parameter between 0 and 1 shows that the model for the adsorption of phenacetin by the adsorbents cannot be reduced to the Langmuir isotherm.

This confirms the hypothesis of the two-parameter isotherm, according to which the Freundlich model is that which best describes the adsorption process. The distribution of residues between $[-2; 2]$, around the x -axis shows that the Freundlich and Redlich-Peterson models are more suitable for describing the adsorption process. The asymmetry at the level of the distribution of residuals around the x -axis suggests that the basic model hypothesis is not followed during the adsorption process, where A_{RP} and B_{RP} are model constants of Redlich-Peterson; β is heterogeneity parameter; A is

Temkin model constant; K_L , Langmuir constant, K_{LF} , Langmuir-Freundlich constant and K_F , Freundlich constant.

3.4. Batch Studies. Pseudo-first order, pseudo-second order, intra-particle diffusion, and Elovich kinetic models were used to investigate and describe the adsorption mechanism. These kinetic models have been presented in non-linear forms (Figure 9) and their calculated parameters are shown in Table 3 below.

The pseudo-first-order model is based on multilayer adsorption on the surface of each adsorbent material. This type of adsorption is based on van der Waal-type interactions between the phenacetin and the copper MOFs. These interactions thus highlight physical adsorption between the adsorbate and the adsorbent. The low values of the error functions of the pseudo-first-order model as well as the coefficient of determination R^2 which tends toward 1 suggest that this model best describes the adsorption of phenacetin by copper (II) fumarate. Also, the pseudo-second-order model highlights π - π interaction between the phenacetin and copper (II) fumarate. These interactions, which are of a chemical nature imply that there is monolayer adsorption. The low values of the error functions of the pseudo-second-order model as well as the coefficient of determination R^2 which tends towards unity plead in favor of this model for the adsorption of phenacetin by copper (II) tartrate. The equilibrium adsorbed amounts, which are close to the experimental amounts in the case of this model suggest that the adsorption of phenacetin by the adsorbents depends on π - π interactions. The Elovich model assumes that the solid surfaces are energetically heterogeneous.

The comparison of the adsorbed quantity of phenacetin from this present work with those obtained from literature are shown in Table 4 below.

By comparing the adsorbed quantities of phenacetin by copper (II) fumarate (25.158 mg/g) and by copper (II) tartrate

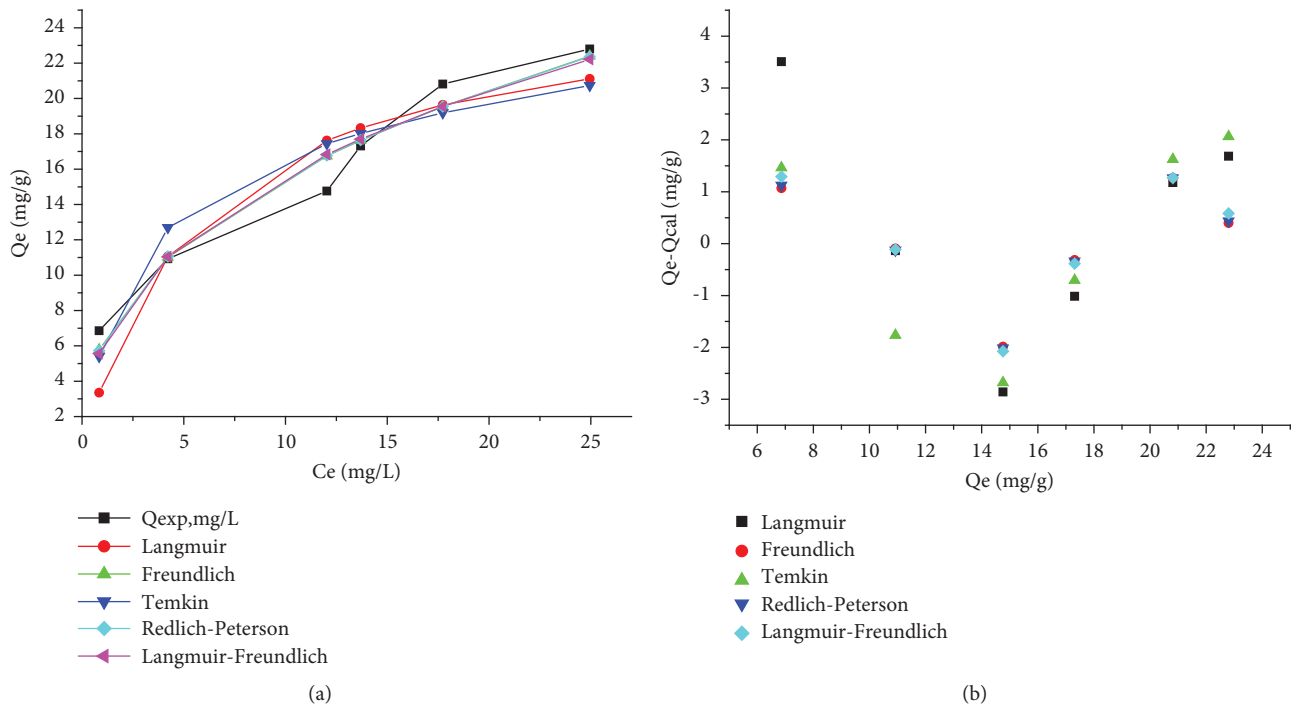


FIGURE 7: Non-linear isotherm (a) and residual (b) plot for copper(II) tartrate (CuTart).

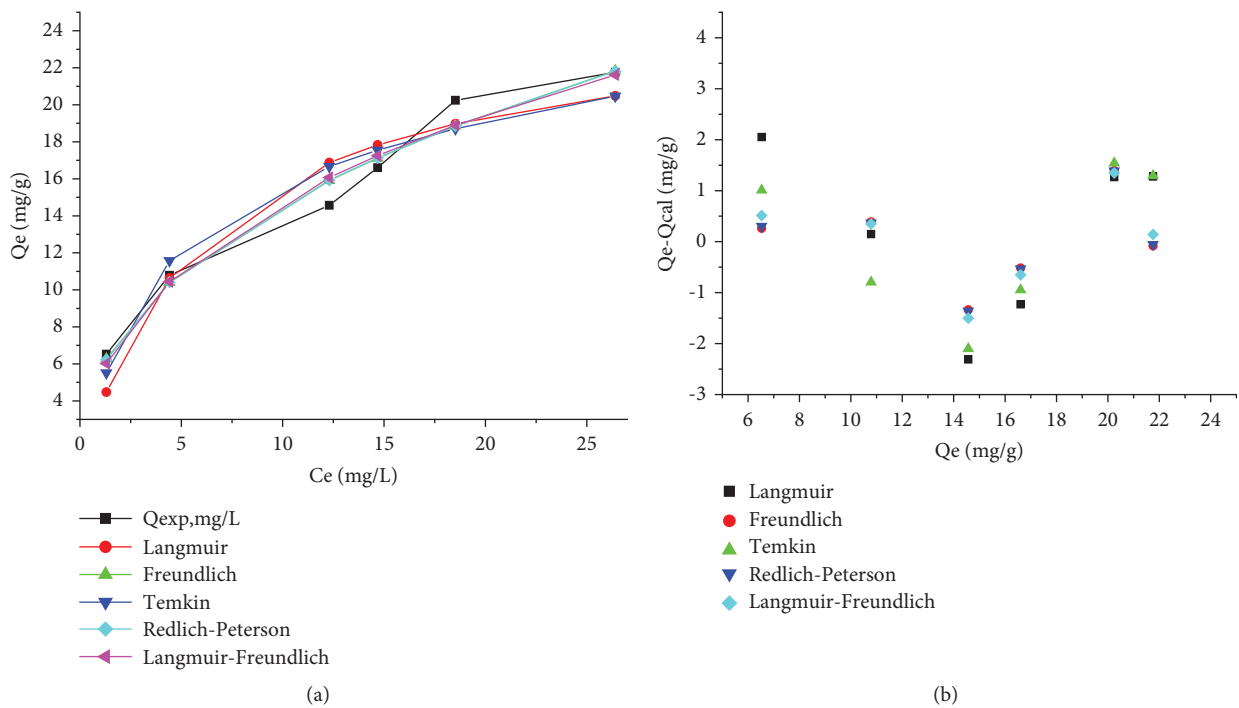


FIGURE 8: Non-linear isotherm (a) and residual (b) plot for copper(II) fumarate (CuFum).

TABLE 2: Adsorption of phenacetin: non-linear fitting analysis for two and three parameter isotherms.

N°	Models	Constants	Values	R^2	SSE	χ^2	ARE	RMSE
CuTart								
1.	Langmuir	Q_m (mg/g) K_L (L/mg)	25.906 0.176	0.899	25.75	4.398	15.109	2.537
2.	Freundlich	$1/n$ K_F (L/g)	0.399 6.204	0.963	6.963	0.529	6.594	1.319
3.	Temkin	ΔQ (kJ/mol) A (L/mg)	547.466 3.920	0.890	19.828	1.424	12.763	2.228
4.	Redlich-peterson	A_{RP} (L.mg ² /g) B_{RP} β	163.981 25.620 0.609	0.962	7.238	0.561	6.850	1.345
5.	Langmuir-freundlich	Q_m (mg/g) K_{LF} (L ^{β} .mg ^{-β}) β	118.358 0.001 0.455	0.959	8.081	0.662	7.466	1.421
CuFum								
6.	Langmuir	Q_m (mg/g) K_L (L/mg)	25.158 0.166	0.929	14.33	1.509	11.370	1.893
7.	Freundlich	$1/n$ K_F (L/g)	0.415 5.611	0.933	4.215	0.256	4.521	1.026
8.	Temkin	ΔQ (kJ/mol) A (L/mg)	498.459 2.326	0.933	11.001	0.764	9.417	1.658
9.	Redlich-peterson	A_{RP} (L.mg ² /g) B_{RP} β	130.178 22.449 0.593	0.975	4.293	0.263	4.618	1.036
10.	Langmuir-freundlich	Q_m (mg/g) K_{LF} (L ^{β} .mg ^{-β}) β	8366 0.004 0.500	0.971	4.897	0.317	5.437	1.106

TABLE 3: Kinetic data obtained by non-linear fitting analysis.

N°	Models	Constants	Values	R^2	SSE	χ^2	ARE	RMSE
CuTart								
1.	Pseudo-first order	Q_e (mg/g) K_1 (1/min)	20.389 0.257	0.809	6.715	0.363	3.606	0.918
2.	Pseudo-second order	Q_e (mg/g) K_2 (g/min.mg)	21.293 0.024	0.940	1.798	0.095	1.862	0.474
3.	Elovich	α (mg/g.min) β (g/mg)	7389.66 0.609	0.854	4.320	0.217	3.049	0.735
4.	Intraparticle diffusion model	K_p (mg/g.min ^{0.5}) C (mg/g)	0.521 16.213	0.679	9.513	0.491	4.72	1.090
CuFum								
1.	Pseudo-first order	Q_e (mg/g) K_1 (1/min)	66.202 0.017	0.986	0.298	0.023	1.056	0.193
2.	Pseudo-second order	Q_e (mg/g) K_2 (g/min.mg)	16.114 0.022	0.925	2.114	1.637	2.854	0.514
3.	Elovich	α (mg/g.min) β (g/mg)	348.238 0.618	0.931	1.818	0.120	2.488	0.476
4.	Intraparticle diffusion model	K_p (mg/g.min ^{0.5}) C (mg/g)	0.540 10.894	0.809	5.122	0.353	4.716	0.800

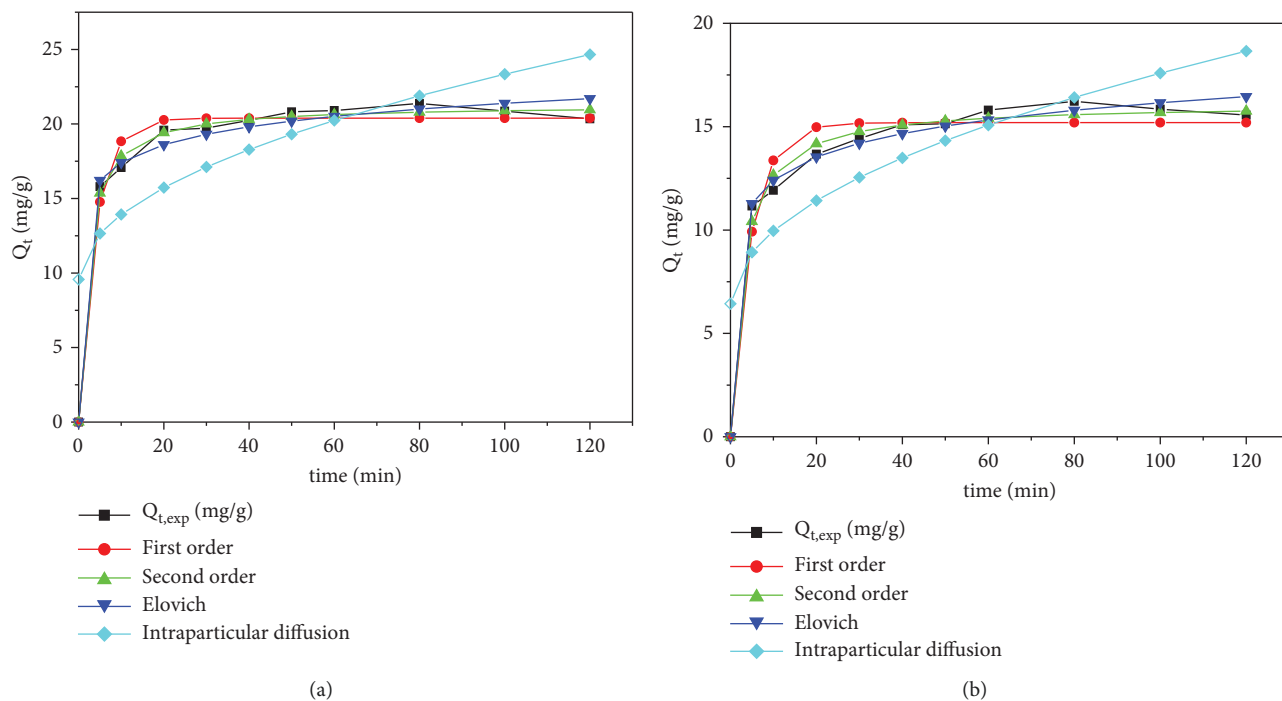


FIGURE 9: Non-linear kinetic adsorption plot onto CuTart (a) and CuFum (b).

TABLE 4: Comparison of adsorption capacity of phenacetin.

Adsorbents	Quantity of phenacetin adsorbed	References
BP1M	13.18 mg/g	[34]
P1M	7.40 mg/g	[34]
B1M	4.11 mg/g	[34]
CuFum	25.158 mg/g	Present work
CuTart	25.906 mg/g	Present work

(25.906 mg/g) and that adsorbed by activated carbons BP1M (13.18 mg/g), P1M (7.40 mg/g) and B1M (4.11 mg/g) [34], the adsorbed quantities obtained from this work is greater than those obtained in the literature. These coordination compounds are potentials adsorbent of phenacetin.

4. Conclusion

In this work, two porous coordination compounds, CuFum and CuTart have been used for the adsorption of phenacetin in an aqueous solution. These compounds were characterized using elemental analysis, IR spectroscopy, thermogravimetric analysis, and powder XRD. The different results obtained enabled us to propose the chemical formulas and then to deduce the structures of the two coordination compounds. Batch adsorption studies showed that increasing the initial concentration of phenacetin enhances the interaction between it and the coordination compounds, resulting in an increase in adsorption capacity. According to the different error functions and coefficients of determination, the kinetic studies show that the adsorption data best fitted by the pseudo-second-order model is more appropriate to describe the adsorption of phenacetin by CuTart, while for CuFum the pseudo-first-order model is the most appropriate. This

indicates that the adsorption of phenacetin on CuTart may be due to chemical interactions while for CuFum it may be due to physical interactions. Isotherm models confirmed that the system is heterogeneous and the adsorption is physical in nature. This study shows that these coordination polymers are suitable for the adsorption of pharmaceutical compounds.

Data Availability

The data used to support the findings of the study can be obtained from the corresponding author upon request.

Conflicts of Interest

The authors have declared no conflicts of interest regarding the publication of this study.

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