Treatment of wastewater from a dairy plant by adsorption using synthesized copper oxide nanoparticles: kinetics and isotherms modeling optimization

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ABSTRACT

Dairy plants produce 1 to 4 L of wastewater per 1 L of processed milk. The wastewater contains high values of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) concentrations, in addition to high levels of dissolved solids. In this study, synthesized copper oxide nanoparticles (CuONPs) coupled with Sophora Japonica fruit, were used as an adsorbent, for the first time, to treat the effluent of dairy plants in a batch adsorption process. The analysis techniques, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized to characterize the adsorbent. The COD removal, using (CuONPs)-based adsorbent, was investigated by varying contact time, masses of the adsorbent, initial COD value and temperatures. The optimum conditions for highest removal percentage were contact time of 120 min, a temperature of 25 °C, pH value of 7.5, and 1 g of adsorbent. The initial COD values used were in the range of 100~700 ppm. The COD percent removal was in the range of 77 to 95%. Freundlich isotherm exhibited the best fitting for the results ($R^2 = 0.998$) with a favorable spontaneous exothermic adsorption process. Based on the calculated normalized deviation value, the modified diffusion model, intra-diffusion, and pseudo-second-order kinetics all showed very good fitting for the adsorption data as indicated by the kinetics study.

Key words | adsorption isotherms and kinetics modeling, adsorption treatment, copper oxide nanoparticle synthesis, optimum COD removal, wastewater dairy plant

HIGHLIGHTS

- A novel synthesis of copper oxide nanoparticles (CuONPs) is made.
- CuONPs are firstly tested for the treatment of wastewater from a dairy plant.
- CuONPs provided high removal ability for COD at the optimized parameters.
- The adsorption is best described by the Freundlich and modified intra-diffusion models.
- The adsorptions process was favorable and spontaneous with an electrostatic adsorption of COD onto CuONPs.

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There are many countries around the world that suffer from the shortage of potable water. Meeting the demand and making fresh water available in some developing countries is costly and takes a lot of effort. Therefore, it can be considered a heavy burden on their budget and a significant challenge to their development and prosperity. Industrial plants consume a big portion of the fresh water supply and usually discharge it contaminated (Hsini et al. 2020). Dairy product plants are among the industries that consume a considerable amount of fresh water; between 1 and 4 L per 1 L of milk. Their effluents are often contaminated with chemicals that cause high biological and chemical oxygen demand values (BOD and COD, respectively) in addition to the existence of suspended solids (TSS) (Kushwaha et al. 2011). Wastewater in dairy plants comes from milk spillage, and as a direct result of using phosphoric, nitric, or sodium hypochlorite solution for cleaning the systems. The effluent can pose a severe threat to the surrounding water and environment if not appropriately treated prior to discharging. Municipal wastewater treatment plants that receive the dairy plants discharge, find it challenging to deal with as it depletes oxygen and forms anaerobic conditions, resulting in foul odors. Upon degrading, soluble and suspended solids in dairy plant effluents release gases and odors, causing eutrophication, form large amounts of fat and high organic content that result in complicating and slowing the treatment process (Sarkar et al. 2006). The harmful effects on human, animals, plants and marine life, caused by the polluted industrial effluents, in addition to the shortage of supplies of fresh water, motivated researchers and scientists to look for practical and low cost methods of treatment during the last few decades. Some of the researches tend to focus on aerobic and anaerobic treatment technologies. Those kinds of treatments usually have some drawbacks such as, but not restricted to, their effect on climate and the need for sludge recycling. Biological methods such as using trickling filters, aerated lagoons, anaerobic filters, and sludge blankets are the most preferred treatment methods for dairy wastewater. These methods consume an ample amount of energy and chemicals. They also require a large space to produce a large volume of sludge and may need to be combined with other techniques to get wastewater completely treated. Physicochemical methods such as coagulation/flocculation, membrane processes, electrocoagulation, electrochemical oxidation, and adsorption are promising and practical treatment methods (Al-Jabari 2017).

Adsorption, one of the treatment techniques, has been studied intensively and reported to be efficient in removing different pollutants from wastewater utilizing different adsorbents (Ba Mohammed et al. 2020; Naciri et al. 2020). The most common adsorbent used is activated carbon. It demonstrated high capacity to remove wide range of organic compounds; however, its cost is relatively high compared to other
adsorbents, and thus remains a primary concern. Therefore, the search for lower cost adsorbent such as rice husk, hay straws, spent leaves, fly ash and synthetic polymers is still ongoing (Benafqir et al. 2020). Metal-based nanoparticles, which are being used in many different fields, have also started to be utilized as an adsorbent recently, motivated by their large surface area, due to the very small particle size, coupled with attractive chemical and optical properties (Theron et al. 2008). Of which copper oxide nanoparticles (CuONPs), often used in biological, agricultural and industrial applications, was investigated as an adsorbent at the nanoparticles size level. It did exhibit positive results in the treatment of wastewater (Peternela et al. 2018). The green synthesis of CuONPs utilizes fruit extracts as a capping agent and copper sources as a precursor. The use of different plant resources, in its synthesis, was claimed to have effects on its properties upon using as an antioxidant, antibacterial, and catalytic (Din et al. 2017). Furthermore, it was investigated in some pharmacological studies as an antifungal against plant pathogens, in solar cells, sensors, and in photocatalytic degradation (Wang et al. 2016).

Detectable COD levels, BOD levels, and solids were found in the effluent of local dairy plants in Amman, Jordan, and was pointed out that treatment is required (Shakhatreh et al. 2015). In this study, syntheses of CuONPs starting with copper acetate monohydrate using local Sophora japonica fruit extract is investigated as a green route to produce an adsorbent. Sophora japonica fruit is available at low cost and with properties that makes it a good candidate for the production of the adsorbent. The study was conducted using nanoparticles of synthesized CuONPs due to the fact that biological studies verified and proved that it is a material with antibacterial activity (Fola et al. 2016). The work aims to explore and understand the potential of using the synthesized nanoparticles of CuONPs as an adsorbent to reduce pollutants in existing wastewater from dairy plants.

**MATERIALS AND METHODS**

**Preparation of Sophora japonica fruit extract**

Sophora japonica fruits were picked from trees in the north of Jordan. They were washed several times with warm deionized water followed by decanting to separate water. Clean fruits were dried in the oven overnight at 60 °C. For further use, the dry fruits were ground using a Retsch mill (RM200) into powder with a size of less than 0.1 mm based on the standard Tyler screening method. 10 g of the fruit powder was mixed with 500 mL deionized water in the Erlenmeyer flask. The mixture was heated at 80 °C with magnetic stirring for half an hour, and the color changed to brown. It was then allowed to cool slowly to room temperature. The liquid was decanted followed by filtration then centrifugation for 10 min at 1,500 rpm in a Pro-Analytical (Centurion Scientific LTD) centrifuge. The final liquid extract was stored in the refrigerator for further use.

**Preparation and characterization of CuONPs**

To prepare the CuONPs, A 200 mL of the aqueous extract from Sophora japonica fruits was added to a 50 mL aqueous solution of copper acetate monohydrate [Cu(CH₂·COO)₂·H₂O] (Alfa Aesar) in a 500 mL Erlenmeyer flask. Deionized water was added to get on the final volume of 500 mL. The concentration of copper acetate was changed from 1 to 10 mM and the volume percentage of the extract was changed from 1 to 10% volume in the different mixtures. The color has changed from blue to green immediately after the addition. The mixture was stirred and heated at 80 °C for 1 h through which the color changed from green to a reddish-brown. The solid precipitate was separated from the solution by decanting and centrifugation. Then it was washed with deionized water followed by ethanol then deionized water, and dried at 60 °C for 1 h. Finally, the solid was calcined at 500–800 °C for the formation of CuONPs.

The formation and characterization of CuONPs were studied. Fourier-transform infrared spectroscopy (FTIR) analysis of the extract and synthesized copper oxide nanoparticles were performed in the range of 4,000–400 cm⁻¹ (IR-Prestige 21 spectrophotometer, Shimadzu) to uncover the interaction of fruit extract with copper and characterize the produced CuONPs. For structure and surface study, X-ray diffraction (XRD) (XRD 6,000 Shimadzu) was run within the range of 5° to 80°. Scanning electron microscopy (SEM) (FEI COUNTA 450 SEM) and size determination was performed using dynamic light scattering unit (Nano-ZS, Malvern, UK) with the standard operating procedure of the instruments (Yugandhar et al. 2017). The surface area of the dried and calcined CuONPs will be measured by applying the Brunauer–Emmett–Teller (BET) adsorption method with N₂ gas. The presence of CuONPs was validated by studying the UV spectrum of the mixture using UV-vis spectrophotometry (JASCO V-700 series).

**Batch adsorption**

Samples of wastewater were collected from the effluent of a dairy plant, filtered and analyzed to determine the
characteristics based on the standard methods (Marshal & Harper 1984). The chemical and physical compositions are shown in Table 1. Samples of 250 mL were diluted with deionized water such that the COD values were in the order of 100, 200, 300, 400, 500 and 700 mg/L. To perform batch adsorption, a measured mass of CuONPs was added to each sample. The samples were then placed on an Orbital shaker (GFL 3,005 orbital shaker) vibrating at 150 rpm. The pH of samples was kept at a value of 7.5 for better removal (Kosmulski 2004). A 250-mL vials containing wastewater sample at a specified pH value, adsorbent mass, and initial COD value were placed in a water bath with a specific temperature, while shaking is taking place, until equilibrium was reached. After the specified time has passed, adsorbent was separated. The solution was analyzed according to the standard methods for the examination of water and wastewater (Rice et al. 2012). The effect of other adsorption parameters such as the adsorbent mass was carried out by increasing adsorbent dose from 0.1 to 1.5 g while keeping other parameters unchanged. Effect of the contact time was investigated at different time intervals by running batch adsorption experiments at a constant temperature, pH, initial COD, adsorbent mass. After each run, the solution was filtered, centrifuged and the supernatant was analyzed to measure the final COD value.

The adsorption-desorption procedure was conducted for the CuONPs using a pre-determined COD concentration of the dairy wastewater. More than 90% of loaded organics were desorbed after 90 minutes and no variations were observed for the longer time. The adsorption capacity of CuONPs reduced slightly, by 9–15%, indicating that CuONPs retains excellent regeneration potential. The consumed particles were washed, for regeneration, in distilled water until the washing-effluent pH became neutral (7.0). The previous steps were carried out in time intervals of 30-minutes and for four hours. At the end of each time interval COD value was measured. The residue of the adsorbed COD on the CuONPs was calculated. Finally, regenerated CuONPs were dried at 105 °C overnight and re-used in the batch adsorption experiments to evaluate their adsorption capacity.

The COD percentage removal (%) and COD adsorption capacity or uptake (q) (mg/g) are calculated from Equations (1) and (2), respectively.

\[
\text{Percentage removal (\%)} = \left(1 - \frac{C_e}{C_0}\right) \times 100 \tag{1}
\]

\[
q = \frac{(C_o - C_t)}{m} \cdot V \tag{2}
\]

where \(m\) is the adsorbent mass (g), \(V\) is solution volume (L), \(C_o\) and \(C_t\) are COD concentration initially and after adsorption in mg/L, respectively. For equilibrium calculations, \(q\) (the dynamic uptake) is replaced with \(q_e\) (the equilibrium uptake, mg/g) and the equilibrium concentration of COD (\(C_e\)) (mg/L) are substituted in relation 2 as shown in Equation (3).

\[
q_e = \frac{(C_o - C_e)}{m} \cdot V \tag{3}
\]

**Adsorption isotherms modeling**

To optimize the adsorption process, adsorption isotherms at equilibrium are necessary to be built and analyzed to describe the interaction of the solute with adsorbent and determine adsorbent capacity. Langmuir isotherm suggests monolayer adsorption with no lateral interaction between the adsorbed molecules. The Freundlich isotherm postulates multi-layer heterogeneous adsorption and is a non-linear model. The Freundlich model and Langmuir model were used in this study to analyze the adsorption results at equilibrium. The Freundlich model is given by Equation (4) and the Langmuir model is given by Equation (5).

\[
\log q_e = \log (k_f) + \frac{1}{n} \log (C_e) \tag{4}
\]

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}k_L} + \frac{1}{q_{\text{max}}k_L} \cdot \frac{1}{C_e} \tag{5}
\]

where \(1/n\) is the exponent of nonlinearity, \(k_f\) is the Freundlich adsorption constant, \(q_e\) is the uptake capacity at equilibrium (mg/L), \(q_{\text{max}}\) is the maximum uptake adsorption uptake in mg/g, and \(k_L\) is the Langmuir adsorption constant (L/mg) (Esseki et al. 2020). The agreement of the experimental data with the Freundlich and Langmuir isotherm models was investigated. Therefore, the best model was selected based on the coefficient of correlation (R²) along

**Table 1 | Chemical and physical properties of wastewater from the dairy plant**

| Property         | COD (mg/L) | BOD (mg/L) | TS (mg/L) | pH  |
|------------------|------------|------------|-----------|-----|
| Dairy plant      | 1,077      | 732        | 760       | 7.5 |
| World bank report| 250        | 50         | 50        | 6–9 |
with the accuracy of obtained $q_e$ from model according to the percentage error in $q_e$ ($\% E_{q_e}$).

### Adsorption kinetics modeling

To investigate the kinetics of adsorption at the different time intervals, the experimental results were analyzed applying the pseudo-first-order kinetics model, the pseudo-second-order kinetics, and the intra-diffusion as given in Equations (6)–(8), respectively.

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -\frac{K_1}{2.303} t$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^t} + \frac{1}{q_e}$$

$$q_t = k_3 t^{0.5} + C$$

where $K_1$ represents the pseudo-first-order kinetics model with constant, $K_2$ is the pseudo-second-order kinetics model constant, $q_e$ (mg/g) is maximum or equilibrium uptake, and constants of the intra-diffusion model are given by $k_3$ and $C$ (Hsini et al. 2020). The modified diffusion model, given in Equation (9), with the constants $k_4$ and $n$ was also investigated.

$$q_t = C_O k_4 t^{1/n} - k_5$$

To find out which model or isotherm that fits the data the best, Equation (10) was used to calculate the normalized deviation $\Delta q$, where $q_{exp}$ is the COD uptake (mg/g) from the experiment, with replicates, and $q_{mod}$ is the COD uptake (mg/g) calculated from each proposed model.

$$\Delta q = \sqrt{n \left( \sum_{i=1}^{n} \frac{(q_{exp} - q_{mod})/q_{exp}^2}{1 - n} \right)}$$

### RESULTS AND DISCUSSION

#### Preparation and characterization of CuONPs

This work evaluated the use of Sophora japonica fruit extract, as a reductant and capping agent, for the synthesis of CuONPs starting with copper acetate monohydrate. The nanoparticles were later used as an adsorbent. Reduction of copper ions to CuONPs is believed to be performed by donation of the hydrogen by flavonoids and chelating of copper ions by phenols. To recognize the assembly of CuONPs, study the part of the extract in synthesis, and get an estimate of possible functional groups and molecules responsible for capping and stabilization of the CuONPs with the Sophora japonica fruits extract, FTIR analysis was applied for the extract and CuONPs as shown in Figure 1. Figure 1(a) presents the FTIR of Sophora japonica fruit extract in the region 400–4,000 cm$^{-1}$ with different peaks indicating the complexity of the extract. The presence of asymmetric hydrogen bounded groups (O-H-stretching) of alcohols, phenols, flavonoids, amines, and amide (N-H) is
shown by a peak at 3,394 cm\(^{-1}\). The –CH\(_2\) and C-H stretching modes in alkanes are assigned at bands at 2,920 cm\(^{-1}\) and 2,846 cm\(^{-1}\), 1,600–1,700 cm\(^{-1}\) is the (O–H bending), and 1,070–1,080 cm\(^{-1}\) is the (C–O stretching) and could be amide carbonyl group. The shoulder peak at 1,739 cm\(^{-1}\) in *Sophora japonica* fruits extract could be attributed to C = C stretching vibrations about C = O amide conjugated C = O of the proteins. Alcohols, phenolic groups, C=N stretching vibrations of aliphatic, and aromatic amines are at the peaks observed in the range of 551–1,519 cm\(^{-1}\). The band at 1,620 cm\(^{-1}\) is for the fruit extract. These peaks are responsible for the capping and stabilization of the CuONPs (Peternela et al. 2018). Peaks at 497 cm\(^{-1}\) and 555 cm\(^{-1}\) represent different types of bending vibration Cu-O bond in Figure 1(b) and the stretching vibration of Cu-O bond is at 1,562 cm\(^{-1}\). In Figure 1(b), peaks for bound (O-H) and (N-H) groups were moved to a higher field at 3,404 cm\(^{-1}\) in the synthesized CuONPs, the peak at 1,384 cm\(^{-1}\) shifted to 1,346 cm\(^{-1}\). These bands were assigned to C-O stretching, C = O stretching and N-H bending. This shift indicates that the coordination of carboxylic acids in the protein, along with other constituents such as: flavonoids, alkaloids, tannins, amino acids, and phenols of *Sophora japonica* fruit extract have a major action in dispersion, stabilization, and capping of CuONPs. The process is suggested to be physical cross-linking between extract and cupper particles since no significant new peaks were noticed in Figure 1(b). Flavonoids and phenols present in *Sophora japonica* fruit extract are the possible synthesizers of CuONPs, where the functional groups like hydroxyl and carbon linkage reduce and cap copper ions into copper nanoparticles (Raul et al. 2014).

Figure 2 shows the XRD results for the synthesized copper oxide nanoparticle in the range of 2\(\theta\) from 20° to 80°. Formation of CuONPs is mainly at 2\(\theta\) value of 38.9° which is consistent with previous work (Johan et al. 2011). The average crystallite size of the synthesized CuONPs was calculated to be in the range 35–100 nm using the Debye-Scherrer equation at the wave length of 0.1541 nm. The average measured BET surface area (a) in the literature is 9.6931 m\(^2\)/g and 25.749 m\(^2\)/g (Geetha et al. 2020). Using the relation \(D = 6/(\Phi \cdot a \cdot \rho)\) with bulk density (\(\rho\)) of 6,300 kg/m\(^3\), shape factor (\(\Phi\)) of 0.5–1, and the measured a, then the obtained diameter of the particles will be in the range 15.0–170.0 nm. Morphology of the synthesized CuONPs, obtained using a scanning electron microscope (SEM), is shown in Figure 3. The particles distributed within a size range of 50 to 120 nm are almost spherical,
others are elliptical in shape, and the rest are agglomerates with larger sizes. The results from the dynamic light scattering of CuONPs showed that CuONPs have an average particle size of 60 nm with zeta potential of 20 mv. The good stability of particles in the liquid medium for particles with a high magnitude of zeta potentials is because of a larger electrostatic repulsion between them. Therefore, CuONPs’ tendency to coagulate or flocculate will be minimized. As a result, the utilization of CuONPs as an adsorbent will be more efficient. The presence of CuNPs was validated by studying the UV spectrum of the mixture using UV-visible-spectrophotometry. When CuONPs absorb light they are excited and results in a distinguished peak. A peak was detected in the range 200–600 nm. It is at 235 nm, as seen in Figure 4 resembling these particles. In addition, a shift to a bigger wavelength is noticed due to the presence of some large particles, and changes in capping agent size and shape (Yugandhar et al. 2017).

Batch adsorption

Effect of contact time

The effect of contact time on the percent removal, for different initial values of COD in the wastewater, is shown in Figure 5. It can be noticed that higher removal rate percentage of COD took place at early time of the process up to a times of about 15 min. The removal percentage continued to increase but at a small rate, and after 120 min no changes are noticed in it. The COD removal percentage for the studied COD values of 100, 300, 500, and 700 mg/L, using 1 g adsorbent in 250 mL, 25 °C and a pH of 7.5, all followed the same behavior. Furthermore, the COD removal percentage was inversely proportional with increasing its initial value while keeping other experimental parameters constant. The higher number of available vacant sites at adsorbent surfaces at early times for adsorption will allow for more pollutant adsorption and as time proceeds these sites become more occupied with adsorbate until equilibrium is reached as found by others (Abdelhay et al. 2017). This explains the high initial adsorption rate.

Effect of adsorbent dosage

Variation of the COD percent removal with the adsorbent dosage (g) is depicted in Figure 6. As the amount of adsorbent increased from 0.1 to 1.0 g, starting with 300 ppm COD value, the percentage removal of COD has increased, and then remained constant. Therefore, an amount of 1 g of adsorbent was used as optimal dosage upon studying effects of the other parameters. The initial increase is due to the availability of more vacant sites on the adsorbent surface. Metal oxide nanoparticles’ adsorption capability with fast removal is mainly due to the high surface area of nanoparticles that leads to high number of reactive sites on the surface, and the lower distance for internal particle

Figure 4 | UV-visible spectrum of synthesized CuONPs using Sophora japonica fruit extract.

Figure 5 | % Removal of COD with contact time (250 mL, pH – 7.5, 1 g adsorbent).

Figure 6 | % Removal of COD at equilibrium using different doses of CuONPs (300 mg/L COD, 250 mL, pH – 7.5).
diffusion. As the adsorbent concentration increases, the distance between particles get smaller and some active sites become blocked (Oladipo et al. 2017).

Effect of initial COD

To investigate effects of the initial COD values on the COD uptake, four different values were utilized (100, 300, 500, and 700 mg/L) as shown in Figure 7. The pH value and temperature were kept constant at 7.5 and 25 °C. The COD uptake increased with increasing the time for each concentration. On the other hand, a larger uptake amount is observed as the initial concentration is increased. This can be related to an increase in the concentration difference which led to an increase in the mass transfer driving force. The highest equilibrium uptake value (96.25 mg/g) was achieved upon using an initial COD value of 500 mg/L, as illustrated in Table 3.

Effect of temperature

The effect of temperature on the percent COD uptake at equilibrium was carried out through using three temperature values (25, 35 and 45 °C) at four different initial COD values (100, 200, 300, 400 and 500 ppm) while the pH value was kept constant at 7.5. Calculated percent removal of COD uptake at equilibrium, at different temperatures is presented in Figure 8. The removal percentage of COD, at equilibrium, by the adsorbent decreased with increasing the temperature for a fixed initial COD concentration. Furthermore, as the initial COD concentration was increased from 100 to 500 ppm, for a fixed temperature, the COD removal percentage, at equilibrium, has decreased. This behavior is exhibited in the case of an exothermic adsorption.

Adsorption isotherms and thermodynamics

Linear fittings of the results obtained, using Langmuir and Freundlich isotherm models, are presented in Figure 9, parts I and II. A summary of the isotherms fitting parameters are given in Tables 2 and 3. Evidently, both models did fit the data very well with correlation coefficient (R²) values greater than 0.97. This suggests that both single and multi-layer adsorption mechanisms were taking place. Table 3 also indicates that, and based on the calculated percentage of uptake at equilibrium, good agreement between experimental and values of qₑ were obtained from the model. On the other hand, although the correlation coefficients were high for both isotherms, calculated normalized deviation percentage (Δq) was higher for Langmuir (11.7) than that of Freundlich (2.5). This indicates that better fitting was represented by Freundlich isotherm than Langmuir, and thus, adsorption was dominated by the multi-layer adsorption mechanism. Freundlich isotherm constants, kᵢ and n are associated with the adsorption capacity and intensity. The calculated values of both constants, as shown in Table 2, indicate good adsorption efficiency; a value for n lying between 1 and 10 indicates favorable adsorption (Kadirvelu et al. 2018). Values of n in Table 2 are greater than 1 suggesting S-type adsorption.

Figure 10 shows results of investigating effect of temperature on the COD uptake at various initial concentrations. Based on the adsorption isotherms results at different temperatures, as specified in Table 2, values of the adsorption capacity constants, Kᵢ and Kᵢ, decreased.
with increasing the temperature, coupled with a decrease in the uptake, consequently, the adsorption reaction can be assumed to be exothermic. Using the correlation

\[ \ln K_L = \frac{-\Delta H}{RT} + A \]

where \( R = 8.314 \text{ J/mol.K} \), \( T \) is the temperature in K, and using \( K_L \) values from Table 3, a plot of \( \ln K_L \) versus \( 1/T \) is shown in Figure 10, and the heat of reaction is calculated from the slope. The Gibbs free energy (\( \Delta G \)) is calculated from \( \Delta G = -RT \ln K_L \). The change in entropy (\( \Delta S \)) is found from \( \Delta S = \frac{\Delta H - \Delta G}{RT} \). A summary of the calculated thermodynamic parameters based on the isotherm fitting is given in Table 4. It can be seen that the calculated heat of reaction along with Gibbs free energy are both negative indicating an exothermic-spontaneous-favorable adsorption process. Also, the value \( R_L \), using

Table 2 | Isotherms fitting parameters for different initial COD values in 250 mL with 1 g adsorbent

| Temperature (K) | Freundlich isotherm | Langmuir isotherm |
|-----------------|---------------------|-------------------|
|                 | \( K_f \) (mg/g) n \( R^2 \) | \( K_L \) (L/mg) \( q_{max} \) (mg/g) \( R^2 \) |
| 298             | 11.95 0.4391 0.9980 | 0.007102 89.29 0.9789 |
| 308             | 8.99 0.4215 0.9832 | 0.003813 80.65 0.9901 |
| 318             | 7.15 0.4008 0.9863 | 0.002906 65.36 0.9852 |

Table 3 | Percentage error in \( q_e \) (\( % E_{q_e} \)) from isotherms fitting

| COD ppm | 298 K | 308 K | 310 K | 298 K | 308 K | 310 K |
|---------|-------|-------|-------|-------|-------|-------|
|         | \( q_e \) Exp. mg/g | \( q_e \) model mg/g | \% \( E_{q_e} \) | \% \( E_{q_e} \) | \% \( E_{q_e} \) | \% \( E_{q_e} \) | \( q_e \) model mg/g | \% \( E_{q_e} \) | \% \( E_{q_e} \) | \% \( E_{q_e} \) |
| 100     | 23.75 | 24.23 | 2.0   | 5.5   | 3.4   | 23.40 | 1.5   | 1.1   | 1.2   |
| 200     | 45.25 | 43.55 | 3.9   | 4.0   | 1.7   | 51.28 | 13.3  | 10.0  | 11.0  |
| 300     | 63.75 | 63.59 | 0.3   | 8.6   | 7.8   | 68.01 | 6.7   | 1.0   | 1.3   |
| 400     | 80.00 | 81.86 | 2.3   | 2.9   | 2.1   | 75.92 | 5.1   | 1.1   | 2.0   |
| 500     | 96.25 | 96.00 | 0.3   | 5.4   | 4.6   | 79.55 | 17.4  | 9.0   | 8.1   |
second-order kinetics have an absolute error in the range (4–7%) which is smaller than that calculated for pseudo-first-order kinetics. Besides, the first-order rate model has lower average R² value, calculated based on all the initial concentrations, than pseudo-second-order model (over 0.99). Therefore, and based on the absolute error percentage and average R² value, the second-order model can be considered to provide better fitting, than the first order model. Curves for fitting the results using the intra-diffusion model and the modified diffusion model are shown in Figure 11.

Based on the kinetic fittings results for the previous models, given in Tables 5 and 6, the calculated values of Δq (%) are 49.0, 7.0, 4.25, and 3.95 for the pseudo-first-order kinetics, the pseudo-second-order kinetics, the intra-diffusion model, and the proposed modified diffusion model, respectively. These findings demonstrate that the pseudo second order kinetics, intra-diffusion model and the modified diffusion model do provide very good fitting for the results obtained, the lowest Δq is corresponding to the best fitting model, over the entire range of concentrations the first order rate law exhibited the largest Δq value. Therefore, the pseudo-first-order kinetics reflected poor fitting as exhibited by the high normalized deviation value.

Regarding the mechanism of adsorption, most of the previous work related to the adsorption of organic pollutants and other material using CuONPs proposed that the adsorption of these materials was due to electrostatic attraction and surface complexation. All the work, in this study, was done at a pH value of 7–7.5, which is less than the isoelectric point of the adsorbent (9–11), which supported the electrostatic attraction and resulted in a higher adsorption capacity. Besides, the excellent fitting of adsorption results supports the ionic interaction between adsorbent and adsorbate (Sharma 2014). The low heat of reaction, given in Table 4 suggests a physical adsorption was involved. Fitting of the intra-diffusion model was tested for adsorption results obtained upon using the 100 mg/L initial COD concentration and result depicted in Figure 12. Obviously, the three successive steps of adsorption are clearly observed as demonstrated by the different slopes that represent the intra-diffusion steps of adsorption are clearly observed as demonstrated in Figure 12. Obviously, the three successive steps of adsorption are clearly observed as demonstrated by the different slopes that represent the intra-diffusion steps. The adsorption of the compounds, which are associated to COD, on the external surface sites of the CuONPs is given by the first step, the second step represents the intra-particle diffusion, and the last step is the equilibrium state at which

### Kinetics of adsorption

To investigate the kinetics of adsorption, fitting the experimental data obtained, using the pseudo-first-order kinetics model and the pseudo-second-order kinetics model, was investigated. Ln (qe-q) versus the time (t) was plotted for first-order kinetics and values of qe and k1 at different concentrations are calculated from the slope and intercept. For the second-order kinetics, q/t versus time (t) was plotted; the intercept and slope were used to calculate k2 and qe. Results from linear kinetics fitting using Excel solver for COD adsorption at different initial concentrations are given in Figure 11, and the parameters are listed in Table 5.

The decrease in the rate constant value, for the second order kinetics, with increasing initial concentration, is an indication of fast uptake rate, and as expected, it remained constant for the first-order kinetics. Both kinetics gave excellent fittings based on the correlation coefficient R² values being greater than 0.94. Nevertheless, calculated values of equilibrium adsorption uptake, based on the pseudo-first-order kinetics have an absolute error in the range (4–7%) which is smaller than that calculated for pseudo-first-order kinetics. Besides, the first-order rate model has lower average R² value, calculated based on all the initial concentrations, than pseudo-second-order model (over 0.99). Therefore, and based on the absolute error percentage and average R² value, the second-order model can be considered to provide better fitting, than the first order model. Curves for fitting the results using the intra-diffusion model and the modified diffusion model are shown in Figure 11.

Based on the kinetic fittings results for the previous models, given in Tables 5 and 6, the calculated values of Δq (%) are 49.0, 7.0, 4.25, and 3.95 for the pseudo-first-order kinetics, the pseudo-second-order kinetics, the intra-diffusion model, and the proposed modified diffusion model, respectively. These findings demonstrate that the pseudo second order kinetics, intra-diffusion model and the modified diffusion model do provide very good fitting for the results obtained, the lowest Δq is corresponding to the best fitting model, over the entire range of concentrations the first order rate law exhibited the largest Δq value. Therefore, the pseudo-first-order kinetics reflected poor fitting as exhibited by the high normalized deviation value.

Regarding the mechanism of adsorption, most of the previous work related to the adsorption of organic pollutants and other material using CuONPs proposed that the adsorption of these materials was due to electrostatic attraction and surface complexation. All the work, in this study, was done at a pH value of 7–7.5, which is less than the isoelectric point of the adsorbent (9–11), which supported the electrostatic attraction and resulted in a higher adsorption capacity. Besides, the excellent fitting of adsorption results supports the ionic interaction between adsorbent and adsorbate (Sharma 2014). The low heat of reaction, given in Table 4 suggests a physical adsorption was involved. Fitting of the intra-diffusion model was tested for adsorption results obtained upon using the 100 mg/L initial COD concentration and result depicted in Figure 12. Obviously, the three successive steps of adsorption are clearly observed as demonstrated by the different slopes that represent the intra-diffusion steps. The adsorption of the compounds, which are associated to COD, on the external surface sites of the CuONPs is given by the first step, the second step represents the intra-particle diffusion, and the last step is the equilibrium state at which
Since Freundlich isotherm expressed excellent fitting for the data, the adsorption mechanism most likely to be a multi-layer. Some studies revealed that adsorption using metal oxide nanoparticles is a multi-step process that includes the adhesion of solute on the outside surface adsorbent then internal particle penetration (Hsini et al. 2020).

Table 5  | Model parameters for pseudo-second-order and pseudo-first-order for different initial COD readings at 25 °C in 250 mL with 1 g adsorbent

| Initial COD (mg/L) | qe (mg/g) (experimental) | k_2^{10^3} (g/mg min) | R^2 | qe (mg/g) model | % error in qe | k_1^{10^2} (1/min) | R^2 | qe (mg/g) model | % error in qe |
|-------------------|-------------------------|-----------------------|-----|-----------------|---------------|-------------------|-----|-----------------|---------------|
| 100               | 23.25                   | 3.492                 | 0.9961 | 25.30          | 6.59           | 2.73              | 0.9488 | 14.34          | 39.6          |
| 300               | 63.75                   | 1.331                 | 0.9983 | 68.49          | 7.40           | 2.77              | 0.9931 | 36.55          | 42.7          |
| 500               | 96.25                   | 0.839                 | 0.9980 | 103.00         | 7.00           | 2.59              | 0.9943 | 55.09          | 42.7          |
| 700               | 122.5                   | 0.647                 | 0.9980 | 131.58         | 7.40           | 2.48              | 0.9886 | 68.64          | 43.0          |

Figure 11  | Kinetics fitting for COD removal using synthesized CuONPs (250 mL, pH = 7.5, and 1 g adsorbent). (a) First-order kinetics, (b) Second-order kinetics, (c) intra-diffusion, (d) modified diffusion model.
Treatment of the wastewater leaving a dairy plant utilizing CuONPs was investigated in this study. CuONPs starting with copper acetate monohydrate and Sophora japonica fruit extract was successfully synthesized for the first time. Analysis techniques including FTIR, XRD, SEM did confirm the presence of CuONPs. The nanoparticles exhibited high adsorption capacity toward reducing the COD value of wastewater discharged from the dairy plant. The highest COD removal percentage, 95%, was achieved upon using a temperature of 25 °C, pH value of 7.5, 1 g of adsorbent and a contact time of 120 min. Freundlich isotherm proved the best fitting for the data obtained with a coefficient of correlation (R²) of 0.998. The negative heat of reaction and Gibbs free, in addition to the inverse proportionality with temperature, are all an indication that the adsorption process is exothermic. The kinetics study indicated that the modified diffusion model, the intra-diffusion model and the pseudo-second-order kinetics all provided excellent fitting for the data with corresponding normalized deviation (Δq) percentage of 3.95, 4.25 and 7.0, respectively. Adsorption mechanism is mainly attributed to electrostatic attraction and hydrogen bonding. In conclusion, synthesized CuONPs exhibited excellent removal efficiency in removing COD-causing matters, with initial COD values between 100 and 700 ppm, from the effluent of a local dairy plant.

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CODE AVAILABILITY

Not applicable.

ETHICS APPROVAL

Accepted principles of ethical and professional conduct have been followed in the research.
DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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