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Investigation of locally available coffee residue as effective adsorbent for dye polluted water treatments

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ABSTRACT

The coffee residues were used as a low-cost and effective adsorbent for the removal of methyl red from aqueous solution. The experiments were performed using operating parameters including initial dye concentration, contact time, solution pH, and adsorbent dosage under batch adsorption technique. The maximum methyl red removal (96.8%) was obtained at pH (2.0), contact time (20 min), initial dye concentration (10 mg/L), and adsorbent dose (0.5 g). The operating parameters such as initial dye concentration, contact time, pH, kinetic study, and adsorbent dosage were conducted; and the adsorption capacities were characterized by using the UV-Visible spectroscopy. The coffee residue before and after adsorption of methyl red was characterized by Fourier transform infrared spectroscopy. The results demonstrated that the coffee residues are very effective, simple, and inexpensive adsorbent in the removal of methyl red from aqueous solution because of its considerable adsorption capacity and abundance. The adsorption isotherms for Langmuir and Freundlich models were determined using the adsorption data. It was found that Freundlich isotherms described very well with the adsorption behavior of methyl red on coffee residue and followed the pseudo-second-order kinetic model.

Keywords: Coffee residues; Operating parameters; Methyl red; Adsorbent; Langmuir and Freundlich models

1. Introduction

Industrialization and urbanization are increasing from time to time in our globe. As a result the risk of environmental pollution increases. Pure water is scarce and is not easily available to all. Deprive sections of the society consume contaminated water and get sick periodically, often resulting in epidemics [1]. The water can be contaminated by natural sources or by industrial effluents. Wastewater is a problem for both developed and developing countries. For example, water pollution due to color from dyestuff is a topic of major concern of scientists today. Organic dyes are widely used in various applications; at the same time these industries also consume substantial volumes of water. Consequently, wastewaters containing dye compounds are discharged in significant amounts, with high concentrations of dissolved organic matter and colorants [2]. A majority of the used dyes such as methyl red are azo dyes which are bright in color due to the presence of one or several azo (—N═N—) groups associated with substituted aromatic structures [3,4]. These dyes or their breakdown products are toxic to living organisms. Furthermore, dyes in wastewater are difficult to remove because they are stable to light, heat, and oxidizing agents and not easily degradable due to the presence of benzene rings [5].

A wide range of chemical/physical and biological treatment methods have been used to remove many dyes [6]. Adsorption technique is one of the noteworthy treatment processes and competitive methods because of high efficiency, economic feasibility, and simplicity of design/operation. It has been proven to be the most suitable and promising technique, and has become the most popularly used technique of depollution because of its effectiveness, operational simplicity, inexpensive, and low energy requirement [7,8].

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Many adsorbents have been tested to reduce dye concentrations from aqueous solutions. For example, activated carbon is regarded as an effective but expensive adsorbent due to its relatively high price, high operating costs, and problems with regeneration hamper its large-scale application. Therefore, there is a growing need of low-cost, renewable, locally available materials as an adsorbent for the removal of dyes. The coffee residue is the chief raw material being studied for this purpose, and they are renewable, usually available in large amounts and potentially less expensive [9,10]. Coffee residues used for low-cost adsorbent are due to their local and abundant availability and the capability to undergo modification to enhance the surface area, adsorption capacity, and range of applicability.

Dye contaminants are present in wastewater from many industries such as textiles, dyeing, cosmetic, chemical, leather, printing, pulp, and paper. Most of the dyes are toxic, mutagenic, and carcinogenic which poses hazard to aquatic life as well as humans and plants [11]. Due to their intense color, they reduce sunlight transmission into water thereby affecting photosynthetic activities of aquatic plants, which ultimately disturb the aquatic ecosystem. They also cause allergic, dermatitis, and skin irritation for living organisms. These problems are the driving force to initiate the researcher to search adsorption of methyl red from aqueous solution using coffee residue. The main purpose of this study was to investigate the removal of methyl red from aqueous solution using coffee residue by batch adsorption technique.

2. Materials and methods

2.1. Chemicals and reagents

Sodium hydroxide (NaOH, MW: 40 g/mol, 98%, from Merck, Germany), sodium bicarbonate ($NaHCO_3$, MW: 84.01 g/mol, from Sigma-Aldrich, Germany), sulfuric acid (H_2SO_4, MW: 98.08 g/mol, >98%, from Breckland Scientific Supplies, UK), acetic acid (CH_3COOH, MW: 60.05 g/mol, >99%, from Sigma-Aldrich, Germany), methyl red ($C_{15}H_{15}N_3O_2$, MW: 269.30 g/mol, from Merck, Germany), and distilled water were obtained from Debre Berhan University Chemistry Laboratory. All chemicals used in this study were of analytical grade.

2.2. Adsorbent preparation

Coffee residue sample was collected from the common coffee house in Debre Berhan town Amhara region, Ethiopia, 130 km far from Addis Ababa. The coffee residues were washed several times with distilled water to remove any color, dust, and other impurities, and dried at 105°C for 24 h in an oven, then ground using mortar and pestle, and sieved to an average particle size (0.355 mm) or 355 µm, finally socked with H_2SO_4 solution 1:1 ratio weight per volume for 3 d to increase surface area and adsorption efficiency. The sample was treated by 0.1 M $NaHCO_3$ till it attained neutral pH and then washed with distilled water in order to remove excess of acid present. The solution was filtered and then the coffee residue was dried at 105°C for 24 h in an oven, then ground and sieved with 355 µm sieve again. The obtained samples were stored in a plastic container for further experimental work.

2.3. Effect of operational parameters on adsorption

2.3.1. Effect of initial dye concentration

Experiments were carried out at different initial concentrations of 10, 20, 30, and 40 mg/L of methyl red solution while the other parameters pH, adsorbent dose, and contact time were kept constant. The absorbance of each sample was measured using a UV-Visible spectrophotometer.

2.3.2. Effect of pH

The effect of pH on adsorption capacities was determined at pH 2, 4, 6, 8, 10, and 12. The pH was adjusted with 10% NaOH and 0.1 M CH_3COOH while the contact time and adsorbent dose was kept constant, and optimum value of initial concentration (10 mg/L) was used. The absorbance of the sample was measured using UV-Visible spectrophotometer.

2.3.3. Effect of adsorbent dose

The adsorbent dose was studied by varying 0.5, 1.0, 1.5, and 2.0 g into the optimum value of initial dye concentration of 60 mL of 10 mg/L solution in 250 mL Erlenmeyer flask and the adsorption efficiency for different dose was determined by keeping contact time constant and optimum value of pH 2.0. The absorbance of the sample was recorded using a UV-Visible spectrophotometer.

2.3.4. Effect of contact time

Experiments were carried out at different contact time by shaking (200 rpm) the sample and coffee residue for 20, 40, 60, and 80 min. The optimum values of initial concentration, solution pH, and adsorbent dose were used. Finally, the absorbance of the sample was recorded using a UV-Visible spectrophotometer.

2.4. Absorbance edge of methyl red

The maximum absorption wavelength (λ_{max}) of methyl red was measured and identified by taking 10 mL of 10 mg/L methyl red solution at different wavelength with the interval of 20 nm from 200 to 800 nm.

2.5. Kinetic studies and adsorption isotherm

Batch adsorption experiments, adsorption isotherm, and kinetic studies were carried out at room temperature. The adsorption kinetic experiments were studied using 60 mL of dye solution of known initial concentration (10 mg/L) was stirred at the constant agitation speed (200 rpm) with a required dose of adsorbents (0.5 g/60 mL) and pH value (2.0) for a specific period of contact time (0, 5, 10, 15, 20, and 25 min) in a shaker. The adsorption isotherm studies were performed by varying the initial methyl red dye concentrations from 10 to 40 mg/L at pH 2.0, shaking time (20 min), adsorbent dose (0.5 g/60 mL), and maintained throughout the experiment. The suspensions were centrifuged and the absorbance was measured using the UV-Visible spectrophotometer. After equilibrium, the final concentrations (C_e) were measured. The percentage removal of the dye was calculated using the following relationship:

$$\% \text{ Removal} = (C_o - C_e)/C_o \times 100\% \quad (1)$$

The amount of methyl red adsorbed per unit mass is calculated as:

$$q_e = (C_o - C_e)V/m \times 100\% \quad (2)$$

where C_o and C_e are the initial and equilibrium methyl red concentrations (mg/L), m is the mass of the adsorbent (g) and V is the volume of the solution (mL), and q_e is the amount of methyl red adsorbed per gram of the adsorbent at equilibrium (mg/g).

3. Results and discussion

3.1. FTIR characterization of coffee residue

The Fourier transform infrared (FTIR) analysis is an important technique to determine the characteristic functional groups for the adsorption of methyl red from aqueous solution using coffee residue, which makes the adsorption behavior possible. The FTIR spectra of coffee residue before and after adsorption of methyl red were illustrated in Figs. 1(a) and (b), respectively. Before adsorption the coffee residue shows some of the absorption peaks, which suggested the complexity of the material. The broad band at 3,425 cm^{-1} was due to the stretching vibration of bonded O–H groups, a band at 2,925 cm^{-1} corresponds to the asymmetrical stretch vibration of $–CH_3$ bond, a very weak band at 2,854 cm^{-1} has symmetrical stretch vibration of $–CH_2$ bond on the surface of coffee residues. The band at 1,295 cm^{-1} was the characteristic of the symmetric bending of $–CH_3$. Before adsorption of methyl red, the coffee residue of FTIR analysis indicated that the presences of carbonyl and hydroxyl groups were included on the surface of the coffee residue, and these groups could be the potential active sites for the removal of methyl red dye. Similar result has been obtained by Ayucitra et al. [12] and Boonamnuayvitaya et al. [13].

3.2. Absorbance edge of methyl red

The maximum absorption wavelength (λ_{max}) of methyl red was found at 410 nm which was used to get the most reliable absorbance position to measure and decrease interference from the equipment as shown in Fig. 2.

3.3. Investigation of adsorption parameters

3.3.1. Effect of initial concentration of methyl red dye

A dosage of 0.5 g of the coffee residue was mixed with 60 mL of each methyl red solutions of different concentrations (10, 20, 30, and 40 mg/L) in conical flask and shaken (200 rpm) for 30 min without adjusting the pH. The absorbance of each concentration was measured after centrifuged the suspension, and percentage removals were determined. The amounts of dye percent removals vs. initial dye concentrations are plotted in Fig. 3. The optimum value of the initial dye concentration was 10 mgL. It was found that an increase in the dye concentration had caused decrease in the percentage of dye removal due to the lack of available active sites required for the high initial concentration of methyl red. Similar results have been reported in the literature [14,15].

3.3.2. Effect of pH

The pH of a solution is an important parameter in the adsorption process. The effect of pH on adsorption of methyl red onto coffee residue was studied at pH 2.0–12.0 as illustrated in Fig. 4. The maximum removal capacity of coffee residue was found to be at pH 2.0. The percentage removal of methyl red increased at the beginning of the pH solution (acidic media), the surface of coffee residue is

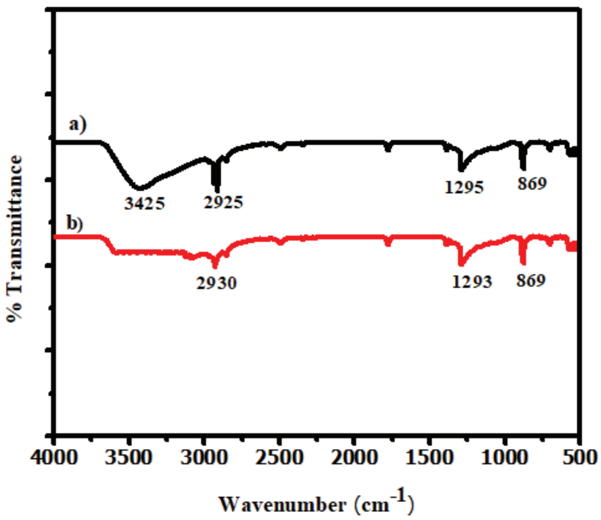

Fig. 1. The FTIR spectra of coffee residue (a) before and (b) after the adsorption of methyl red.

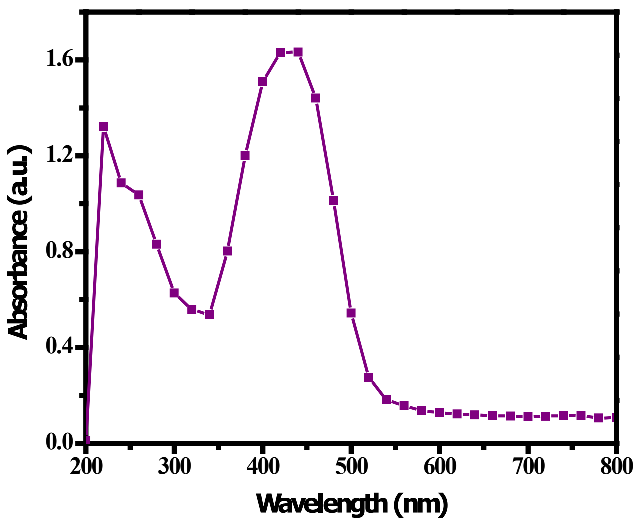

Fig. 2. The maximum absorption wavelength/absorption edge of methyl red dye.

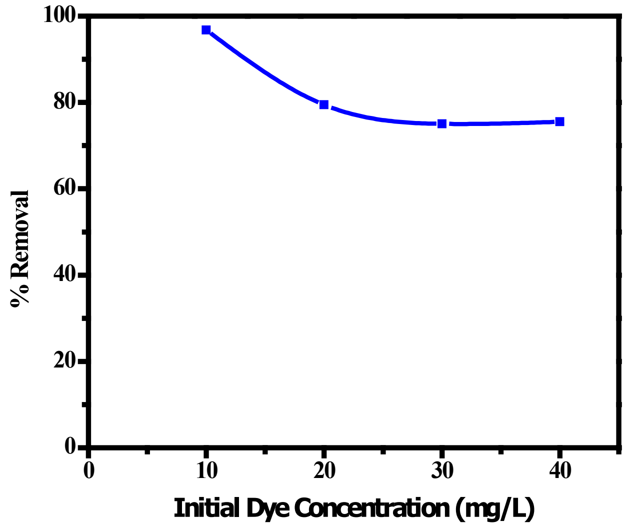

Fig. 3. Effect of initial concentration of methyl red dye.

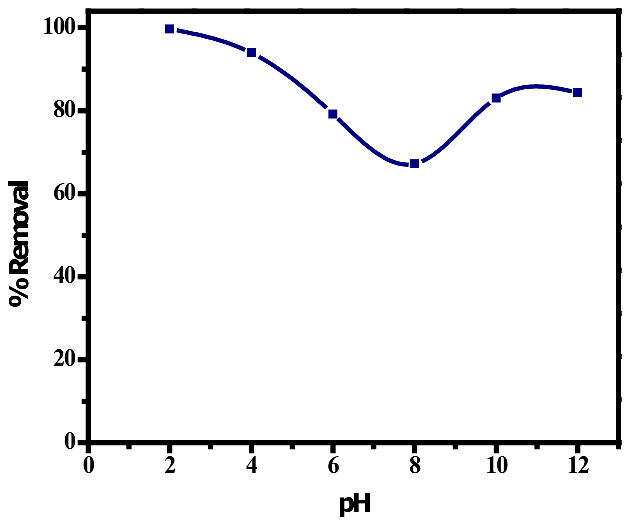

Fig. 4. Effect of pH on the adsorption of methyl red dye.

negatively charged at lower pH. Significantly strong electrostatic attraction appears between the negatively charged coffee residue adsorbent and the cationic methyl red molecule leading to maximum adsorption, while the pH value increased the attraction between oppositely charged adsorbate and adsorbent which ultimately leads to the reduction in adsorption capacity [16]. Initial pH value may enhance or depress the uptake. This is attributed to the charge of the adsorbent surface with the change in pH value. The decrease in adsorption capacity in the basic region is due to the decrease in positive charges of the coffee residue and increase in competition of ions with the OH^-. The increase in the adsorption of the dye with decreasing pH values is due to the attraction between the azo dye and excess H^+ ions in the solution [17,18].

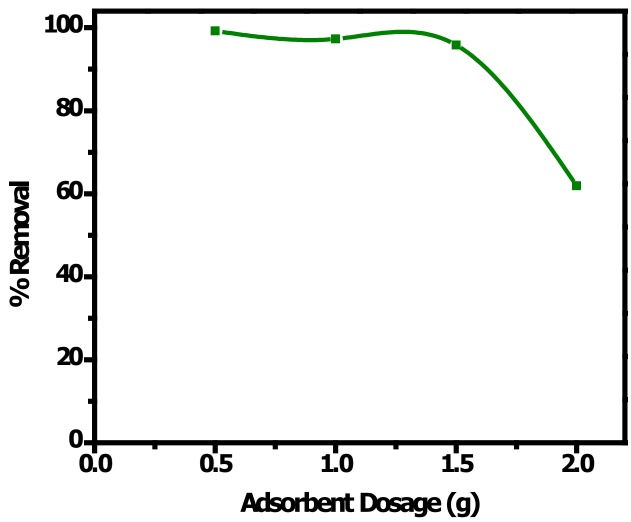

Fig. 5. Effect of dose of adsorbent on the removal of methyl red.

3.3.3. Effect of adsorbent dose

The optimum dose of coffee residue (0.5 g) on the adsorption of methyl red is shown in Fig. 5. So as the amount of adsorbent coffee residue increases the removal efficiency also increases with some continuous variation. As the dosage of adsorbent increases the adsorption increases proportionately. The increase of dosage increases adsorbent sites thus contact surface area with the dyes increases. Therefore, the amount of dye uptake increases and consequently leads to a better adsorption. The decrease in the efficiency at higher adsorbent dosage may be attributed to the overcrowding of adsorbate molecules which prevent the diffusion through the actual adsorption sites [14,19].

3.3.4. Effect of contact time

To investigate the effect of contact time, an experiment was carried out by mixing using shaker and the optimum value of 60 mL of methyl red solution of 10 mg/L concentration with 0.5 g coffee residue (20, 40, 60, and 80 min) with agitation speed of 200 rpm at pH 2.0. After centrifuge the absorbance was measured at each time and the percentage removals of methyl red was determined. The effect of contact time on the adsorption of methyl red onto coffee residue is represented in a plot of percentage adsorption vs. contact time as shown in Fig. 6. The adsorption rate was rapid during the first 20 min (optimum) due to the highly negatively charged surface of the coffee residue for the adsorption of methyl red in the solution at pH 2.0 and then continued at a slower rate from 20 to 80 min. This was due to the fact that, at the initial stage the number of free adsorption sites was higher, and the slow adsorption rate in the later stage was due to slower diffusion of solute into the interior of the adsorbent [20].

3.4. Adsorption isotherm

Adsorption isotherm describes the equilibrium of the adsorption materials at a surface at constant temperature.

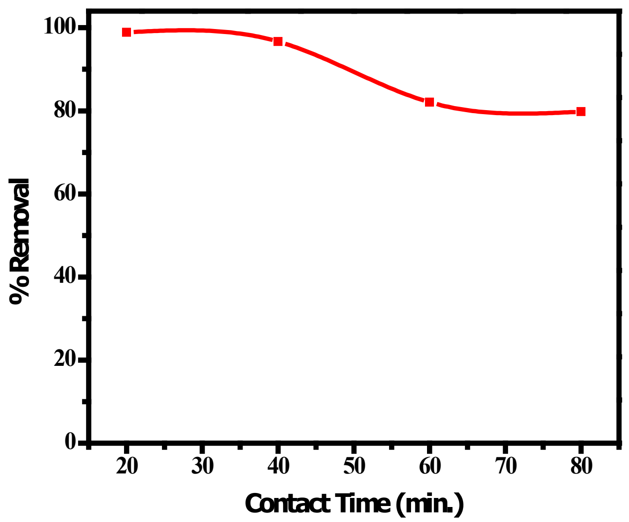

Fig. 6. Effect of contact time on the removal of methyl red.

The isotherm results were carried out by containing methyl red dye with 0.5 g/60 mL of adsorbent for 20 min at different initial concentrations ranged from 10 to 40 mg/L at room temperature. Fig. 7 shows the adsorption isotherms for methyl red by coffee residue adsorbent. The relative parameters of each isotherm were obtained according to the intercept and slope from the plots of C_e/q_e vs. C_e and log q_e vs. log C_e, respectively, and their correlation coefficients (R^2) from the linear isotherm model are illustrated in Table 1. The Langmuir model assumes that the adsorbent surface contains energetically homogenous cites, where the monolayer surface coverage is formed with no interactions between the molecules adsorbed [21]. The Langmuir isotherm is represented by the following linear equation:

$$C_e/q_e = 1/q_m b + C_e/q_m \quad (3)$$

where q_e is the amount of methyl red adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), q_m is the measurement of the adsorption capacity (mg/g) based on Langmuir isotherm, and b is the Langmuir constant. From the plot of C_e/q_e vs. C_e (Fig. 7(b)), a straight line was obtained with a slope value of 0.2829 giving q_m values of 3.535 mg/g and an intercept of 0.4547 giving b value of 0.622. The values of R_L are found to be 0.064 in Table 1, conforming that the feasibility of the adsorption isotherm in between 0 and 1 indicating a favorable adsorption. This means that adsorbate in solution have tended to be adsorbed on the coffee residue adsorbent.

The Freundlich isotherm model considers multilayer and heterogeneous surface adsorption and the exponential distribution of sites and their energies [22]. The linearized form of the equation is:

$$\log q_e = \log K_f + \tfrac{1}{n} \log C_e \quad (4)$$

where K_f (mg/g)(L/g)^n and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

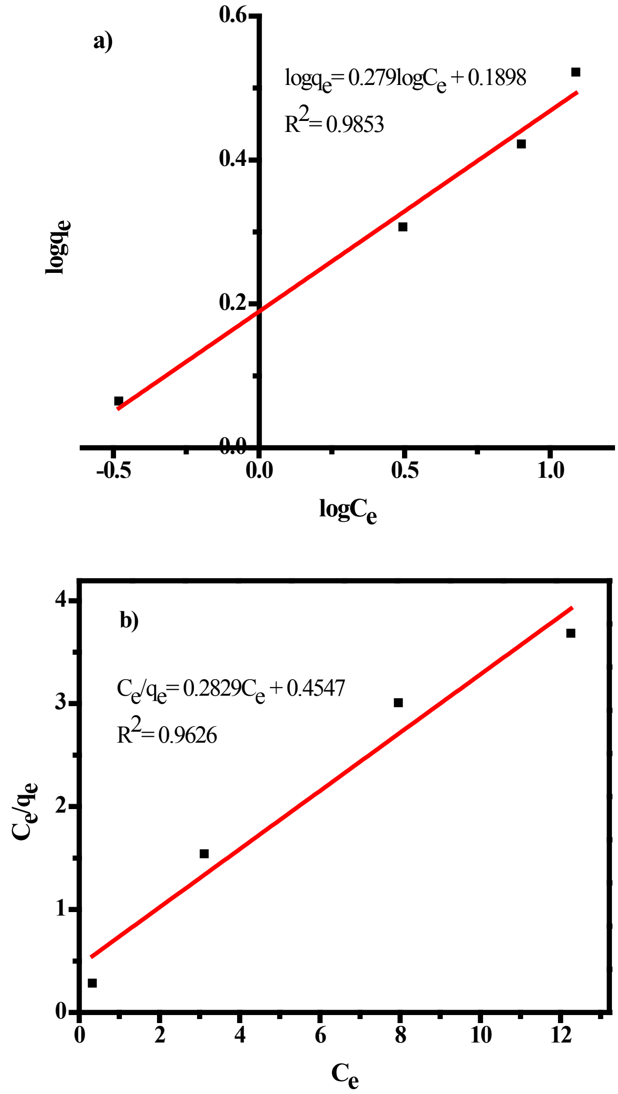

Fig. 7. Freundlich (a) and Langmuir (b) adsorption isotherm of methyl red by coffee residue adsorbent at (C_o = 10 mg/L, pH = 2.0, adsorbent dose = 0.5 g/60 mL, time = 20 min and at room temperature).

Plotting log q_e vs. log C_e (Fig. 7(a)) provides a straight line with a slope of 0.279 and an intercept of 0.1898. The value of 1/n lying between 0 and 1, which is 0.279 and the n value lying between 1 and 10, which is 3.584, shows a favorable condition for sorption. The Langmuir's and Freundlich's plots were interpreted with respect to correlation coefficient (R^2), a statistical measure of how well the regression line approximates the real adsorption data (Table 1). In this study, the adsorption isotherm of the coffee residue adsorbent showed better fit to Freundlich than the Langmuir isotherms model (i.e., 0.985 vs. 0.963, respectively). Conformation of the experimental data to the Freundlich isotherm model means the heterogeneous nature of adsorbent surface; that is, each dye molecule/adsorbent surface adsorption sites are not equivalent and there are interactions between adsorbent molecule and adjacent sites [23].

Table 1
Langmuir and Freundlich isotherm constants for methyl red adsorption by coffee residue

Adsorbent	Langmuir model				Freundlich model		
Coffee residue	q_m (mg/g)	b	R_L	R^2	K_f	$1/n$	R^2
	3.535	0.622	0.064	0.9626	1.548	0.279	0.9853

3.5. Adsorption kinetics

The study of adsorption kinetics is very useful for understanding the involved mechanisms and also useful for the design of future large-scale adsorption facilities. The controlling mechanism of the adsorption process was investigated by fitting pseudo-first-order and pseudo-second-order kinetic models to the experimental data [24] and these models are used in our study.

3.5.1. Pseudo-first-order kinetic model

This model was suggested for the sorption of solid/liquid systems. It can be expressed as:

$$\log(q_e - q_t) = \log(q_e) - k_1 / 2.303 \tag{5}$$

where q_e and q_t are the amount of dye adsorbed on adsorbent (mg/g) at equilibrium and at time t (min), respectively, and k_1 (1/min) is the rate constant of pseudo-first-order kinetics.

3.5.2. Pseudo-second-order kinetic model

It was assumed that the rate-limiting step might be the chemical adsorption, in which concentrations of both adsorbate and adsorbent were involved. If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation after integration is expressed as:

$$t/q_t = 1/k_2 q_e^{\,2} + t/q_e \tag{6}$$

The kinetics of methyl red adsorption from aqueous solution by using coffee residue is depicted in Fig. 8. The kinetic adsorptions, which are helpful for the prediction of maximum adsorption rate, give important information for designing and modeling the adsorption processes. It was found that 96.8% removal of methyl red concentration occurred in the first 20 min, thereafter the rate of adsorption becomes slow.

The kinetics studies of methyl red dye from aqueous solution onto the coffee residue as shown in Fig. 9. Adsorption kinetics describes the rate of adsorbate uptake governing the contact time of adsorption reaction [22]. The pseudo-second-order kinetic plot for the adsorption of methyl red onto coffee residue is presented in Fig. 9. The results showed that the adsorption process followed a pseudo-second-order kinetic model, based on the kinetic parameters and high correlation coefficient values in Table 2. Further, compared with experimental results (1.189 mg/g), the values of theoretical results (2.046 mg/g) for the pseudo-second-order model were much more reasonable than those for the pseudo-first-order model due to the experimental (1.189 mg/g) and theoretical

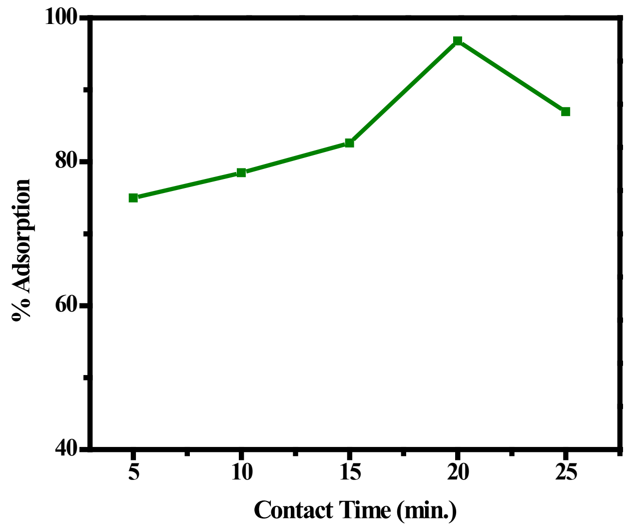

Fig. 8. Kinetic adsorption on the removal of methyl red dye (C_o = 10 mg/L, pH = 2.0, adsorbent dose = 0.5 g/60 mL and at room temperature).

(11.12 mg/g) adsorbed mass at equilibrium is very low. Most of the theoretical values of the pseudo-first-order model deviated significantly from the experimental values.

Table 3 illustrates, the comparison of maximum percentage removal and adsorption capacities (q_m) of the adsorbents, which were obtained from both Langmuir and Freundlich isotherm models, with other adsorbents in literatures. It is clearly shows that the adsorption capacity of coffee residue for the removal of methyl red is higher than as compared with other reported adsorbents.

The use of low-cost, locally available, and eco-friendly adsorbents has been investigated as an alternative to the current expensive adsorbent for methyl red dye removal from aqueous solution and also there is a great concern to reduce the pollution arising from industrial influents. For that reason, it is necessary to focus on the excess locally available agricultural wastes such as biochar from coffee grounds, sugarcane bagasse pith, activated carbon, *Posidonia oceanica* (*L.*) fibers, mango bark, neem bark, citrus waste, coffee residue, etc. Among those, coffee residue is one of an effective adsorbent for methyl red adsorption and as a result, their profitable utilization and adding value of these unused materials used for the applications of dye polluted water treatment [28]. This work also has investigated the methyl red adsorption onto economical and efficient adsorbents for wastewater treatment. The coffee residue has become one of the most cost-effective, low operation cost, locally available, and highly efficient adsorbent for the adsorption of methyl red dye from aqueous solution as compared with other adsorbents in Table 3.

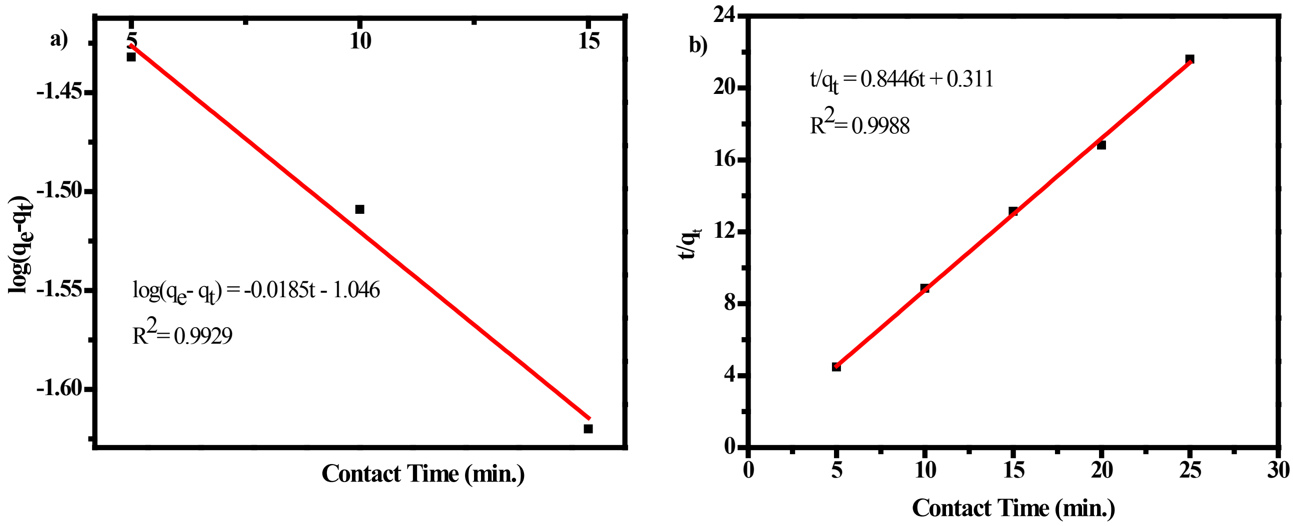

Fig. 9. Plot of pseudo-first-order (a) and pseudo-second-order model (b) (C_o = 10 mg/L, pH = 2, adsorbent dose = 0.5 g and at room temperature).

Table 2
The values of parameters and correlation coefficients of kinetic models

Experimental	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
q_e	k_1	q_e	R^2	k_2	q_e	R^2
1.189	0.043	11.12	0.9929	1.945	2.046	0.9988

Table 3
Comparison of the maximum % removal and adsorption capacities (mg g^{-1}) of effective adsorbent for dye removal from wastewater

Adsorbent	Dye	% Removal	q_m (mg/g)	Reference
Sugarcane bagasse pith	Methyl red	86.00	–	[25]
Coffee residues	Methyl red	86.30	–	[26]
Coffee residue	Methyl red	93.50	–	[26]
Activated carbon	Methyl red	82.81	–	[17]
Posidonia oceanica (*L.*) fibers	Methylene blue	–	0.44	[27]
Mango bark	Malachite green	69.76	0.50	[15]
Neem bark	Malachite green	–	0.36	[15]
Sawdust	Phenol	–	0.0221	[20]
Coffee residue	Methyl red	96.80	3.54	This work

4. Conclusion

This study is focused on the removal of methyl red using inexpensive and locally available coffee residue from aqueous solution. The operating parameters such as initial methyl red concentration, pH, adsorbent dose, and contact time were well optimized and effective on the removal efficiency of methyl red. The maximum removal efficiency of coffee residue was found as 96.8% for 10 mg/L methyl red solution, 0.5 g/60 mL adsorbent dose, pH solution 2.0, and contact time at 30 min. The experimental data were analyzed by using Langmuir and Freundlich adsorption isotherm models and the correlation coefficients for Langmuir and Freundlich equations are fitted well. The adsorption isotherm behavior is described by a multilayer Freundlich isotherm model and the kinetic study of methyl red on coffee residue was performed based on the pseudo-first-order and pseudo-second-order equations. The data indicates that the adsorption kinetics follow the pseudo-second–order equation. Based on the results of this study, it can be concluded that the coffee residue adsorbent is an effective, low-cost, easily available, and alternative adsorbent for removal of methyl red from aqueous solution because of its considerable adsorption capacity.

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Conflict of interest

The author declares that there was no conflict of interest.

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