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Biosorption of Ciprofloxacin (CIP) using the Waste of Extraction Process of Microalgae: The Equilibrium Isotherm and Kinetic Study

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Abstract

Scientists are investigating the efficacy of different biosorbents for promoting economic and environmental viability in purifying contaminants. Among the primary by-products of biodiesel production is waste microalgae biomass, which has the potential to be used as a cheap biosorbent for the treatment of pollution. In the present study, the biomass left over after extracting the chlorella vulgaris was used to test the potential biosorption of CIP from simulated aqueous solutions. Bisorbent's ability was characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). Analysis with a Fourier Transform Infrared Spectrometer revealed that CIP biosorption occurred mainly at biomass sites containing carboxyl and amino groups. The equilibrium isotherm data and biosorption kinetics were addressed in the present study. The biosorption data match the Langmuir isotherm model, and the maximal biosorption capacity was determined to be 7.56 mg/g. While The pseudo-second-order model accurately described the biosorption kinetic data. Biosorbent regeneration was also studied using two different sodium hydroxide concentrations, the results showing that after desorption, the biosorption capacity decreased from 5.2 to 3.74 and 1.77 (mg/g) using 0.1NaOH and 0.5NaOH, respectively.

Keywords: Microalgae; waste Chlorella Vulgaris biomass; Biosorption; wastewater treatment; Ciprofloxacin.

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1- Introduction

Over the past ten years, attention to pharmaceuticals in the aquatic cycle has increased [1, 2]. Pharmaceutical substances frequently prevent or treat various illnesses in humans and animals [3]. These substances are eliminated in the urine and feces as the original substance or a combination of metabolites called pharmaceutical compounds (PhCs). Partial breakdown often leaves behind metabolites that are just as hazardous or even more physiologically active than the original medication [4, 5]. Therefore many kinds of pharmaceutical contaminants such as hormonal substances, antimicrobial agents, antacids, anesthesia, medication for inflammation, antipyretics, beta-blockers, tranquilizers, energizers, and fatty acids-lowering drugs have been found in drainage effluents [6]. Following their discharge into sewage systems, these chemicals are used in liquid services for waste treatment, where it is necessary to reduce pathogens, organic pregnancy, nitrogen, and phosphorous [7]. Antibiotics are a class of organic chemicals that, through various biochemical effects, can inhibit the growth or metabolic activity of bacteria. The lateral metabolic processes of microorganisms either produce them or are chemically or semi-artificially synthesized [8]. Most antibiotics in the environment are discharged from homes, hospitals, and pharmaceutical factories. The potential risks to human and ecological health posed by antibiotics found in aquatic environments from such sources are viewed as a new and serious problem [9] .Conventional wastewater treatment facilities are unable to remove antibiotics and microorganisms [10]. As a result, the rise of antimicrobial resistance (AMR) will probably culminate in ten million deaths and a 2-3.5 percent decrease in the gross domestic product by 2050 [11]. Antibiotics can be divided into subgroups, including ß-lactams, quinolones, tetracyclines, macrolides, sulphonamides, and others. These complex chemicals may have several functions inside a single molecule. Depending on the pH, they can be neutral, cationic, anionic, or zwitterionic [12]. Quinolones are a class of antibiotics with a core bicyclic arrangement connected to the chemical formula 4-quinolone [13]. Fluoroquinolone-resistant bacteria are becoming more common due to the excessive use of these drugs and environmental pollution [14]. Among the fluoroquinolone antibiotics, Ciprofloxacin is the most commonly prescribed drug

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worldwide. It is followed by ofloxacin, levofloxacin, lomefloxacin, norfloxacin, and sparfloxacin. While it is still widely used in Europe, norfloxacin has been taken off the market in the United States [15]. Bayer A.G. invented Ciprofloxacin in 1983 and was authorized by the U.S. Food and Drug Administration (USFDA) in 1987. Antibacterial Ciprofloxacin treats various bacterial infections, including those of the urination tract and lungs [16, 17]. Due to their ability to survive for extended periods in sewage treatment plants and subsequently re-enter the watery environment, CIP creates a serious threat to the population's health. It has unfavorable effects on photosynthesis and aquatic life, in addition to encouraging the emergence of antibiotic-resistant bacteria [18, 19]. The concentration of Ciprofloxacin in the environment might be anything from ngL^{-1} to mgL^{-1}. The concentration in pharmaceutical wastewater reached 31 mgL^{-1} [20]. Ciprofloxacin elimination from water has been researched using physicochemical techniques, such as ozonation [21]. Oxidation is catalyzed by light [22]. In addition to adsorption [23, 24]. furthermore, Ion-exchange, membrane separation, Photodegradation and Photo-Fenton [25-28]. The most promising of these technologies is adsorption due to its inexpensive price, high performance, flexible design, and simplicity of use [29]. The kind of adsorbent used is one of the most crucial aspects of the adsorption process. Many studies have suggested various adsorbents, among that are organic, inorganic and agricultural wastes [30]. Toxins in wastewater streams can be effectively removed using living and dead biomass, such as marine algae, bacteria, fungi, and yeast [31]. Dead biomass has many advantages, such as the lack of required growth conditions and nutrients in the feed solution, the ease of biosorption, and the ease of biomass regeneration and reuse [32]. The microalgae source was deemed to be the best option to address environmental issues because it produces more biofuel than other sources [33]. Optimising the potential for effective microalgae cultivation., it has been suggested that residual microalgae biomass could extract pollutants from the water after lipid extraction [34]. The primary objective of this study is to combine experimental and theoretical methods to investigate the equilibrium isotherms and kinetics of CIP biosorption onto extracted biomass (C. vulgaris).The following that the impact of biosorbent characterization (FTTR, SEM, EDX) on the biosorption mechanism was investigated.

2- Materials and Methods

2.1. Reagents

The regional AL KINDI pharmaceutical industries Company provided the Ciprofloxacin (CIP) antibiotic, C17H18FN3O3 (cleanliness greater than 98%, molecular weight M.W.: 331.3 g/mol). Other chemical compounds included chloroform (CHCL3, purity 99.0%, M.W.: 119.38), which Alpha Chemika in India procured, and ethanol (C2H60, purity 99.7%, MW 46.07) from (THOMAS BAKER.INDIA).

2.2. Preparation of Stock

Concentrate solutions of Ciprofloxacin (CIP) were prepared by disappearing the necessary quantity of the antibiotic in distilled water, which were then diluted to the required concentrations. To maintain the proper pH in the antibiotic solution, sodium hydroxide (0.1 M) and hydrogen chloride (0.1 M) solutions were made.

2.3. Biomass Preparation for Biosorption

Bulk supplements in Henderson, USAC, supplied Chlorella Vulgaris (C.Vulgaris). The biosorbent used in this study was obtained from the waste biomass of green microalgae. To extract the bioactive components from the marine green microalga C. vulgaris, a Soxhlet extractor was used with organic solvents (ethanol and chloroform, respectively). The remaining biomass was rinsed several times with purified water to eliminate most remaining particles of solvents. The biomass was crushed and used after being dehydrated in a 40 degrees Celsius dryer. Our previous work describes the detailed procedure of the extracted biomass [35]. Fig. 1 demonstrates how biomass is transformed during the extraction process.

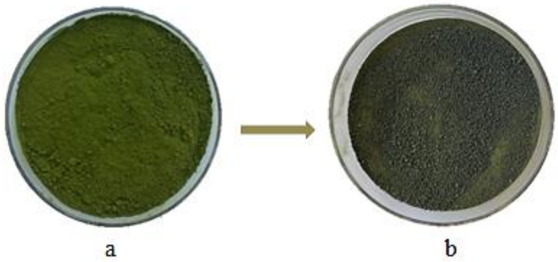


Fig. 1. Raw Biomass of Chlorella Vulgaris (a) and Chlorella Vulgaris biomass after extraction (b)

2.4. Biosorbent Characteristics

The biomass of C. Vulgaris was examined using a Fourier transform infrared (ATR, 1800, SHIMADZU, Japan) spectrum analyser. This analytical technique used a KBr disc between 400 and 4000 cm^{-1} to determine the functional groups on the surface of a C. vulgaris biomass sample. Next, the scanning electron microscopy technique (FESEM-EDS, MIRA III, TESCAN, Czech) explained the microalgae biosorbent's morphology. Finally, the fundamental composition of bio adsorbents has been identified using an elemental scanner (Xflash 6110; Burkercompany; Germany).

2.5. The Biosorption Isotherm for CIP

The optimal experimental parameters were selected based on the results [35]. Biosorption tests were conducted in 200 ml Duran flasks. Each bottle contains fifty milliliters of CIP buffer with a starting concentration

ranging from 50 to 600 mg/L to analyse CIP biosorption equilibrium isotherms on C.Vulgaris biomass extracts. The acidity of the resulting solutions was adjusted by adding either sodium hydroxide (0.1 M) or hydrogen chloride (0.1 M) in small amounts. Each bottle received 2.75 g of biomass added to it and was shaken at 200 rpm at room temperature for 120 minutes to ensure equilibrium was reached. The biosorbent was separated from the aqueous phase by centrifuging a 10 mL sample and filtering it through 0.2 m membrane filters. Using the HPLC chromatography model SYKAMN, researchers at the Ministry of Science and Technology's research center and investigating food contamination/environment and water determined the final CIP concentration. It had a 100 l injection valve, using a C18 reversible analyzing column (25 cm * 4.6 mm and 3.5 m) and a UV/Vis detector set to 278 nm. At a 1.0 ml/min flow rate, the mobile phase was a titrated mixture of (A=0.025 M phosphoric acid modified to pH 3 with triethanolamine, B=acetonitrile, C=methanol) (40: 40: 20).
The following expression determined the equilibrium CIP biosorption capacity, q_e (mg/g).

$$q_e = \frac{(C_i - C_e)}{m} \times v \tag{1}$$

C_i and C_e are the ciprofloxacin concentrations (mg/L) at the initial and end of the adsorption process. At the same time, m is the mass (g) of the biosorbent, and V is the volume (L) of the ciprofloxacin solution in contact with the sorbent.

2.6. Kinesis of Biosorption of CIP

Kinetic tests followed the same protocol as equilibrium experiments. CIP adsorption kinetic was determined at different times (10, 30, 50, 70, and 90 minutes)**,** and CIP concentrations were measured in the same way. Adsorbed CIP concentration (qt) (mg/g) at time t was determined by:

$$q_t = \frac{(C_i - C_t)}{m} \times v \tag{2}$$

When t minutes have passed, the concentration of CIP solution in the liquid phase is denoted by C_t (mg/L) (min).

2.7. Studies of Desorption and Regeneration

CIP desorption was carried out to regenerate the waste C.Vulgaris biomass by following the desorption protocol suggested by [36]. After the biosorption tests, the CIP-loaded waste C. vulgaris biomass was dried at 40 degrees Celsius and brought into contact with various NaOH solutions. The Duran samples contained 2.75 g of biomass and 50 ml of NaOH with different concentrations (0.1, 0.5 M) sharked for 1.5 hours on a rotary shaker (200 rpm) at room temperature. Deionized water was used to wash the biomass until the wash solution's pH reached seven. For reuse, the biomass was crushed after being dried at 40 °C.

3- Mathematical Modelling

3.1. Langmuir Isotherm

Maximum adsorption occurs when a single saturated layer of the solute molecules covers the surface of the adsorbent, the adsorption energy is steady, and no adsorbate molecules migrate along the adsorbent's exterior, as predicted by the theoretical Langmuir sorption isotherm [37]. Langmuir absorbency isotherm is depicted in Eq. 3 and expressed in Eq. 4 linearly.

$$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_L} \frac{1}{C_e} \tag{4}$$

Where C_e (in millimolar / liters) is the equilibrium of the remainder concentration, q_m(in milligrams per gram) is the greatest amount of adsorption for the solid phase loading, and K_L (in liters per milligram) is an energetic static associated with the thermal capacity of biosorption. The Langmuir plot of 1/ C_e versus 1/ q_e was used to determine the q_m and K_L [38].

The parameter for equilibrium R_L is a dimensionless constant that can be used to define the fundamental properties of the Langmuir isotherm. It is also known as the separation factor. R_L was determined using Eq. 5 [39].

$$R_L = \frac{1}{1 + (1 + K_L C_o)} \tag{5}$$

C_o = starting concentration, K_L = adsorption energy constant (Langmuir Constant). If R_L is greater than 1, adsorption is unfavorable; if R_L is equal to 1, it is linear; if R_L is less than 1, it is favorable. And if R_L is zero, it is irreversible.

3.2. The Freundlich Isotherm

According to the Freundlich isotherm model [40]+, adsorption is a mechanism that occurs through surfaces with heterogeneity and is mediated by multi-layer adsorption . Linear Freundlich isotherm expression using Eq. 6:

$$\log q_e = log K_F + 1/\, n \log C_e \tag{6}$$

K_F is the bond energy-related Freundlich constant (mg/g) (l/mg). The adsorption or distribution coefficient, denoted by the K_F, is the amount of CIP adsorbed onto an adsorbent per unit equilibrium concentration. Adsorption that deviates from a linear relationship has a heterogeneity factor of 1/n. The value represents the deviation of the solution concentration from a linear relationship with adsorption. When n=1, adsorption is linear; when n is less than 1, adsorption is a chemical process; and when n is greater than 1, adsorption is a preferred physical process [41].

3.3. The Temkin Isotherm

The Temkin isotherm model explicitly modifies adsorbing species-adsorbate interactions [41]. Some of the presumptions made by this model are as follows: For all molecules in the layer, the heat of adsorption decreases linearly with coverage due to interactions between the adsorbent and the adsorbate, and (ii) binding energies have a uniform distribution up to a certain maximum energy to bind. Furthermore, The Freundlich equation implies that the decline in the sorption heat is logarithmic; however, the Temkin isotherm assumes that it is linear. The Temkin model can be described as follows:

$$q_e = B \ln (K_T C_e) \qquad (7)$$

Rearranging this results in the following:

$$qe = B \ln K_T + B \ln C_e \qquad (8)$$

K_T is the equilibrium bind constant (L/mg) that indicates the highest binding energy, and B is a constant related to the heat of adsorption. $q_e$versus lnC on a graph to calculate K_T and B [42], and B can be determined by Eq. 9.

$$B = \frac{RT}{b_T} \qquad (9)$$

Where b_T (K.J. mol $^{-1}$) is the constant linked with the sorption of the heat for exothermic (b_T > 1) or endothermic (b_T 1) sorption reactions, the constant R for gases is 8.314 J mol^{-1} K^{-1}, and T is the absolute temperature [43].

3.4. Dubinin–Radushkevich Isotherm

The following equation, developed by Dubinin and Radushkevich [44], is another well-liked the formula for analyzing isotherms with a high degree of rectangularity has the form given below:

$$q_e = qme^{-\beta\varepsilon^{2}} \qquad (10)$$

In this equation, q_m represents the Dubinin-Radushkevich single layer capability (mg/g), β (mol^2 /kJ^2) is a constant associated with absorbing energy, and ε is the Polanyi potential associated with the state of equilibrium concentration according to the following:

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \qquad (11)$$

R reflects the gas constant (8.314 J/mol.K), C_e the equilibrium concentration (mg/l), and T is the absolute temperature value. The relationship between the constant β and the mean free energy (E, kJ mol^{-1}) of sorption per sorbate molecule when it is transported from infinity in the solution to the surface solid is shown in the equation below:

$$E = \frac{1}{\sqrt{2B}} \qquad (12)$$

3.5. Models for Kinetics

Several kinetics models, including pseudo-first-order and pseudo-second-order kinetic equations, as well as intraparticle diffusion kinetic equations, could be applied to the experimental data to learn more about the mechanisms of control in adsorption processes like mass transfer and chemical reaction [45].

3.5.1. Pseudo-First-order Kinetic Model

The first-rate formula for absorbing a liquid/solid system with reliable capacity was the Lagergren rate equation, which describes the physical bonding of pollutants onto the surface of a biosorbent [46]. Equality of pseudo-first order by Lagergren.

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (13)$$

Consequently, to be used in the kinetic analysis, Eq. 13 is linearised as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (14)$$

where q_e and q_t are the equilibrium and time-dependent adsorption capacities in mg/g, respectively, and k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant.

3.5.2. Pseudo Second-order Equation

Ho's pseudo-second-order kinetics model considers the chemisorption adsorption rate as the rate-limiting step [47]. The equation can be written as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (15)$$

To convert Eq. 15 to a linear form, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e} t \qquad (16)$$

The letter k_2 (g/mg.min) symbolises the pseudo-second-order sorption rate constant. the k_2, R ^{2}, and q_{cal} values. It is possible to identify the linear relationship by examining the plot of t/q t vs t produced by Eq. 16.

3.5.3. Intraparticle Diffusion Model

The ability to reliably identify the rate-control phase in a sorption process is paramount. In film diffusion, a thin liquid film carries the solute from the bulk solution to the adsorbent's surface. After that, the adsorbate molecules attach to the sorbent's active sites. Finally, The sorbent absorbs the solute through intraparticle diffusion, which travels through the sorbent's pores and binds to the material's active sites [48]. A model of intraparticle distribution based on the concept formulated by Weber and Morris was tested, allowing us to determine the diffusion mechanism [49]. Biosorption processes typically share an empirically observed functional connection where uptake varies roughly proportionally with t ½ rather than using the contact time t. Describes the intraparticle diffusion mechanism shown in Eq. 17:

$$q_t = k_p t^{½} + C \tag{17}$$

C is the intercept, and k_p is the intraparticle diffusion rate constant (mg/gmin½), which can be derived from the slope of the q_t versus $t^{½}$ Linear plot.

4- Discussing the Results

4.1. Characteristics of Biosorbents

4.1.1. FT-IR

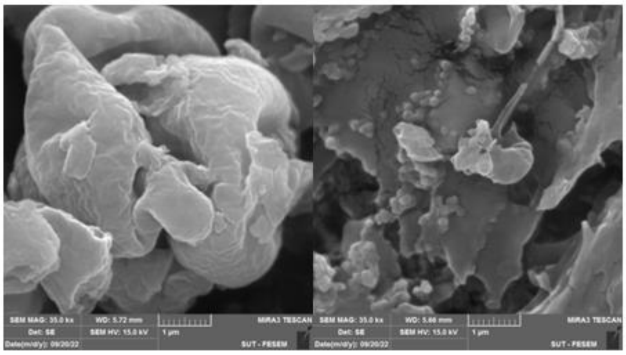
FT-IR spectroscopy investigated the interactions between CIP ions and the extracted C. vulgaris biomass. The primary bands typical of the functions group are listed in Table 1.

4.1.2. SEM- EDX

Scanning Electron Microscopy (SEM) analysis was used to observe the textural characteristics of the biomass surface. Fig. 2A illustrates that The cells in the unextracted biomass sample appeared completely and clumped together to form a sphere [56]. Fig. 2B revealed that the cells had cracked and distorted surfaces. Some microalgal cell structures were altered by Soxhlet extraction, while others remained unaffected, and the membrane cell showed no signs of harm, agree with [57]. Also, the biomass exhibits numerous free particles of a substance, which could give the biomass more contact surface, similar to [58]. According to EDX analysis (Fig. 3a), the primary elements in original C.vulgaris biomass are carbon (63 %), oxygen (13.08%), and nitrogen (18.98%). Additionally, Minor elements include Mg, P, and Ca (1.25%, 2.43%, and 1.21%, respectively), close to what was reported by [59]. A slightly different composition was displayed (Fig. 3b) due to the chemical processes used in extraction. Carbon (61.7%), oxygen (7.09%), and nitrogen (28.1%) were the major chemical elements. While the trace elements P (1.54), Mg (0.91), and Ca(0.65) [36].

Table 1. FTIR Functional Groups and Spectral Bands for Wasted C.Vulgaris Biomass

Wavenumber (cm^{-1})	attribution	bands of absorption (cm^{-1})
3448.72 3278.99	correlated with stretching vibrations of O-H and N-H [50]	3029-3639
2927.94	Lipids and carbohydrates had strong C-H vibrations [51]	2809-3012
1654.92, 1543.05	Modes of vibration for amide I and amide II (protein fraction) [52]	1583-1709
1234.44	Atomic acid (other phosphate-containing compounds) Vas> P=0 phosphodiester stretching [53]	1191-1356
1022.27	Polysaccharide carbohydrates with the formula V(C-O-C) [54]	980-1072
1458.18	Aromatic compounds C=C	1600–1420
1076.28	Alcohols, phenols, ethers C-O [55]	1300–950



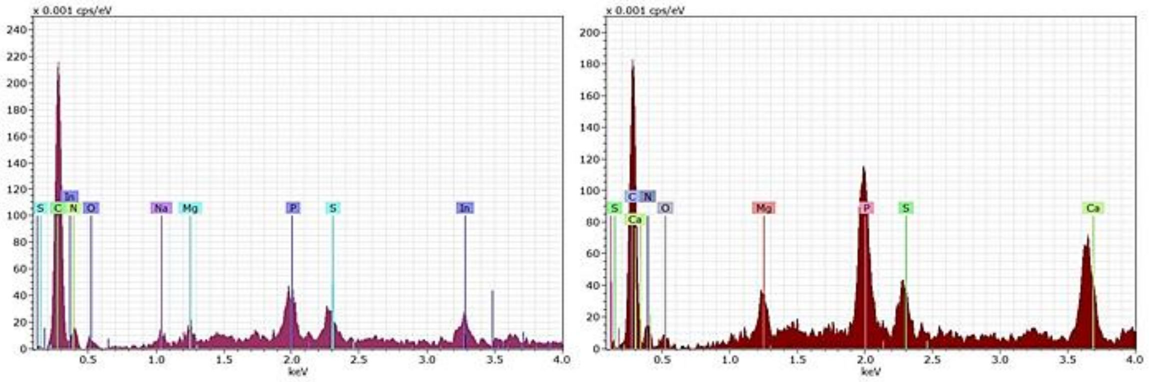
A B

Fig. 2. SEM Image of Original C.Vulgaris Biomass (A) and Waste C.Vulgaris Biomass (B)

4.2. Mechanisms of Biosorption for CIP

In general, the characterization and variable studied above may support the mechanism of removal of microalgae waste. The CIP ions are attached to the biomass by a complex process involving many techniques, including ion exchange, surface precipitation, and surface complexation, as shown in Fig. 4. Because of concentration gradients, CIP ions diffuse across the cell wall and membrane before being attached to the biomass [60, 61]. In particular, this is because the biomass's cell wall contains a variety of functional groups, including amines, carboxyls, hydroxyls, phosphates, sulfhydryls, etc. The FTIR analysis supported this explanation and was agreed upon by [62]. The binding of CIP to microorganisms via biosorption relies on several different mechanisms. Some of these mechanisms include ion exchange due to polysaccharides present on the cell wall of the microorganism, which contain ions like+, Ca2+, P and Mg^{2+}The presence of elements is demonstrated through analysis EDX, and physical Biosorption due to Van der Waal's force. Comparable behavior to the results obtained by [63]. Electrostatic, hydrophobic, hydrogen-bonding, and - electron donor-acceptor interactions with CIP are all made possible by the carboxylates on the surface of dead biomass. In addition, CIP+ can be absorbable through ion exchange H+, and mineral ions can be shifted out for CIP+ during an ion exchange [64].

Additionally, pH. plays a crucial role in the biosorption procedure. Acid dissociation constants for CIP are pKa1 and pKa2, which are 6.1 and 8.7, respectively [65]. CIP molecules mainly exist as cations (CIP+) due to the amine group in the piperazine moiety being protonated at pH 6.1; at pH values greater than 8.7, the carboxyl group of CIP molecules loses a proton, transforming the molecule into an anion (CIP) [66, 67].



a
b

Fig. 3. EDX of Original C.Vulgaris Biomass (a) and Waste C.Vulgaris Biomass (b)

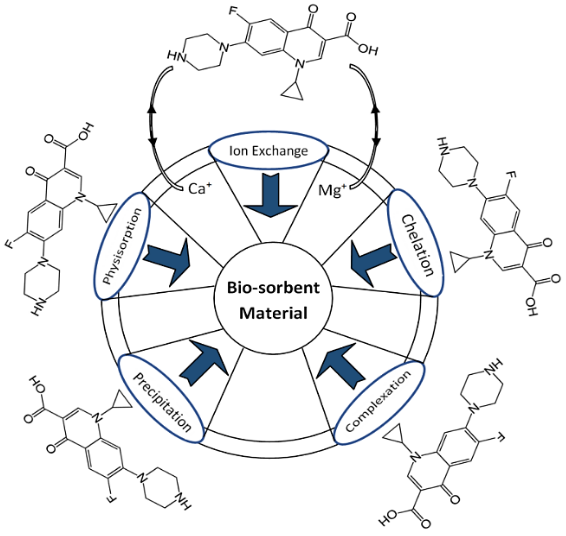


Fig. 4. Mechanisms for the Biosorption of CIP. Several Mechanisms Include Chemical Binding (complexation, chelation), Ion Exchange, Physisorption, and Precipitation

4.3. CIP Biosorption Isotherms

Understanding the forces influencing the adsorbate and biosorbent interaction is essential for optimizing biosorption. A proper equilibrium correlation must be established to compare different adsorption systems' ability to remove pollutants [68]. The equilibrium data have been correlated with four different isotherm models: Authors like Langmuir, Freundlich, Temkin, and Dubinin-Radushkevichd. The optimal isotherm to describe the biosorption process was determined by comparing their R^2 values. Fig. 5 shows different isotherm model plots. Table 2 displays the results of the biosorption models utilized in this investigation.

The Langmuir isotherm R^2 value from the biosorption models was 0.9949. This result demonstrates that the isotherm model fits the experimental data well. Found similar outcomes [69]. The Langmuir isotherm assumes the surface is covered by a monolayer of adsorbate when maximal monolayer biosorption has occurred. This biosorption isotherm can determine the optimal biosorption capacity that matches monolayer coverage on C. vulgaris biomass [70]. The extracted C. vulgaris had a maximum biosorption capacity of 7.56 mg/g, which is approximately the experimental biosorption capacity of 6.8 mg/g [71]. The separation factor (R_L) value ranged from zero to unity, indicating that the procedure was favorable and the data were well-fit to the Langmuir isotherm [72]. The Freundlich model's result of $n > 1$ indicates that the sorption process was simple, good, and physical [73]. The sorption reaction is exothermic if $b_T > 1$ and endothermic if b_T 1. In the concentration range studied, the b_T value for C.Vulgaris biomass was a positive number, indicating that the process was exothermic [43]. The Dubinin-Radushkevich model's calculated apparent energy of sorption, E, can be utilised to make educated guesses about the sorption mechanism. The sorption type is considered physical if this value is less than eight kJ mol^{-1}. The process is chemisorption if the activation energy is between 8 and 16 kJ mol^{-1}. The findings suggest that the Biosorption of C. vulgaris is a physical process following [74].

Table 2. The Parameters for Each Isotherm Model Utilized in the Experiments

Isotherm model	**Parameter**	**R^2**
Langmuir	q_m (mg/g)= 7.565 K_L (L/mg) = 0.006 R_L=0.081	0.994
Freundlich	K_F[(mg/g) (l/mg) ¹⁄n]= 0.144 n= 1.595	0.886
Temkin	K_T(L/mg) =0.152 b_T (KJ mol^{-1}) =1.630	0.813
Dubinin–Radushkevich	q_m(mg/g)= 3.442 β= 64.125 E(kJ mol^{-1}) = 0.088	0.832

4.4. CIP Biosorption Kinetics

Various kinetic models, including pseudo-first-order, pseudo-second-order, and intraparticle diffusion, aid the biosorption rate for extracted C.Vulgaris biomass. Fig. 6 illustrate the practical data acquired from the kinetic investigation to remove CIP ions from aqueous solutions using C. vulgaris. Table 3 shows the results of fitting the experimental data, including the parameters of kinetics and correlation coefficients.

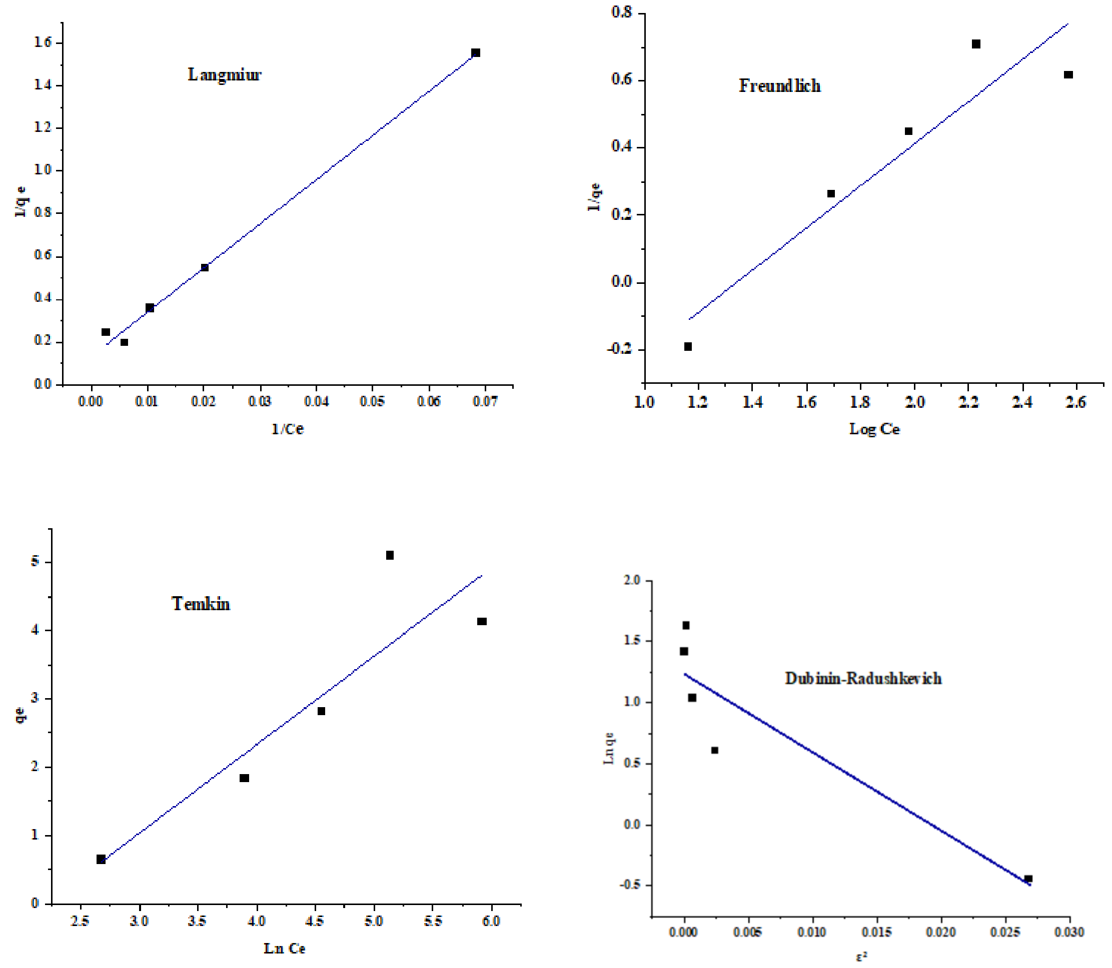


Fig. 5. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherm Models for Biosorption on Waste C.Vulgaris Biomass

Table 3. The Kinetics Constants for CIP Biosorption by Waste C. Vulgaris Biomass

Experimental	**First order kinetic**			**Second order kinetic**			**Intraparticle diffusion**		
q_{exp} (mg g^{-1})	k_1 (min^{-1})	q_e(mg g^{-1})	R^2	k_2 (g $mmol^{-1}min^{-1}$)	q_e (mg g^{-1})	R^2	k_p(mg/g. min½)	C	R^2
5.368	0.007	3.719	0.923	0.006	4.340	0.990	0.278	0.575	0.973

The results showed that the pseudo-second-order model had a better determination of the coefficient (R2: 0.9908) than the pseudo-first-order model (R2:0.9234). The capability of biosorption calculated using the model of second order agrees well with the experimental value (qexp.= 5.368 mg/g), which is higher than the value predicted by the model of pseudo-first order (qe cal. = 4.34046 mg/g) [75], These findings prove that the biosorption of CIP ionic onto C. vulgaris Biomass proceeds according to a pseudo-second-order kinetics approach. This model assumes that chemical biosorption, which involves valence forces through the sharing or exchange of the electrons between the sorbent and the sorbate, is the limitation step. The findings were consistent across researchers [76, 77]. The adsorption rate may be constrained only by intraparticle diffusion if the plot is straight and passes through the origin. Alternatively, the adsorption could be regulated by a number of different factors [78]. Fig. 6 exhibits a linear relationship. Since the model's generated graph does not pass through the beginning point, the intra-particle diffusion process is the adsorption mechanism, although additional agents are in operation [79]. The boundary layer's impact is represented by the intercept of the plot. Higher intercepts indicate that rate-limiting surface sorption is more critical [44].

4.5. Compared to Other Adsorbents

Table 4 compares the adsorption capacity values of the extracted C. vulgaris to the CIP adsorption capacities reported for various other adsorbents (activated carbon, agricultural waste, clay organic residues, etc.). The CIP removal capacity of the extracted biomass (C.Vulgaris) was more significant than or comparable to kaolinite, agricultural residues, and organic waste. Extracted C. vulgaris had a lower CIP removal capacity than activated carbon, modified biomass, and NH-DGS. However, its lower cost and economic efficiency make it a compelling alternative [80].

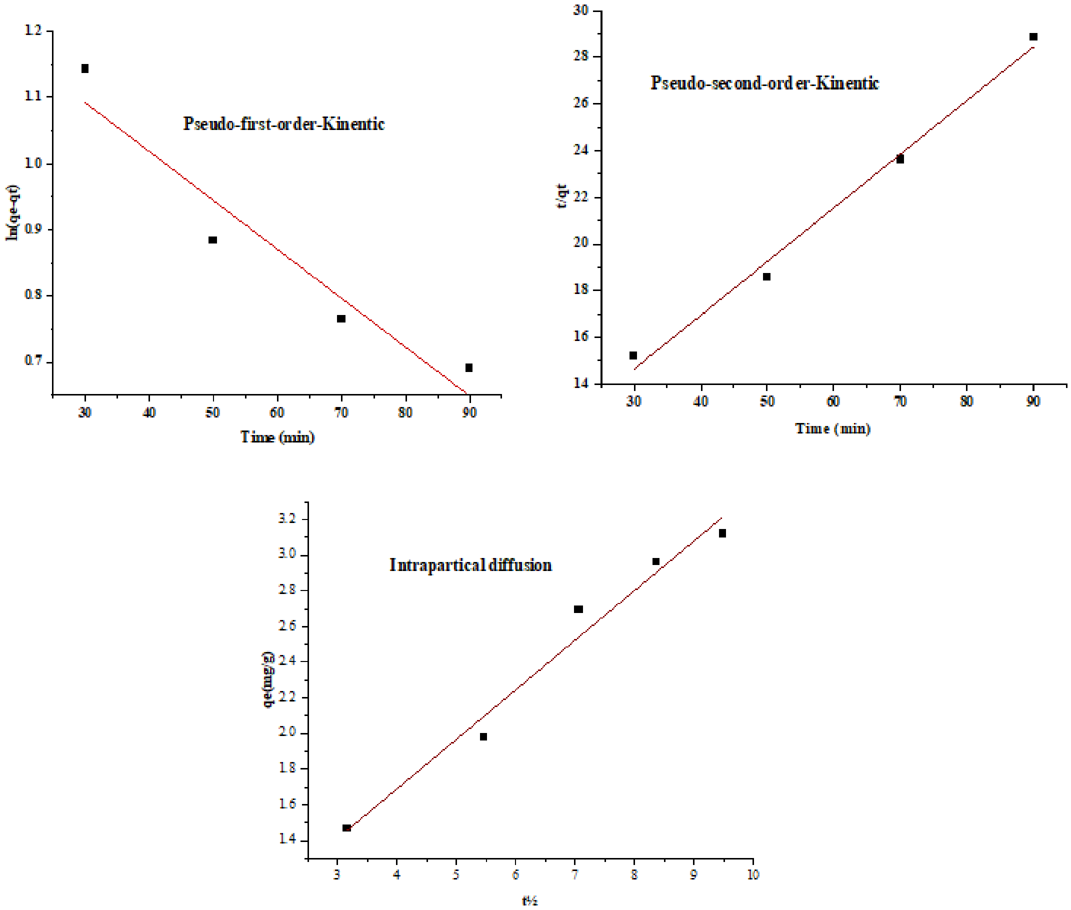


Fig. 6. Kinetic Models Implemented to Describe the CIP Adsorption on the Waste C.Vulgaris Adsorbent

Table 4. A Study Comparing the Removal of CIP using C. Vulgaris Biomass Waste and other Adsorbents

No.	**adsorbent**	**Adsorption capacity (mg/g)**	**Conditions pH, initial concentractio,temperture**	**Ref**
1	modified biomass of green alga Scenedesmus obliquus	39	pH: 7 I.C:50 mg/l	[81]
2	Activated carbon from the banana stalk	49.7	pH: 8 T:323K I.C:50 mg/l	[82]
3	*Dialium guineense* seed waste (DGS) modified by sodium hydroxide form	9.17	pH: 6 I.C:100 mg/l	[83]
	NH-DGS 120.34	120.34		
4	activated sludge (AS)	3.39	PH: 7 I.C: 300 ng mL^{-1}	[84]
5	organic residues: cor cob (CC)	13.76	PH: 6 I.C: 60 mg L^{-1}	[85]
	rice husk (R.H.)	2.33		
6	biocomposite of 50% regenerated-reed (R.R.) and 50% need charcoal (ChR)	17.3	pH:10.42 I.C :75 mg/L	[86]
7	modified coal fly ash	1.55	pH: not adjusted T:313K I.C:100 mg/l	[87]
8	kaolinite	6.3	pH :3 to 11 IC 0.2–1.0 mM	[88]
9	extracted biomass(C.Vulgaris)	6.8	pH :7 I.C:450 mg/l	This study

4.6. Studies of Desorption and Regeneration

Reusing biosorbents after removing CIP from aqueous solutions is a cost-effective option. Biosorbent regeneration efficiency using a single cycle of desorption agent was investigated in this study. Saturated biomass is regenerated by adding NaOH at varying concentrations and then compared to the unregenerated adsorbent. Fig. 7 shows that the biosorption capacity declined from 5.2 to 3.74 and 1.77 (mg/g) using 0.1M NaOH and 0.5M NaOH, respectively, after desorption. The progressive degradation of the biomass and unfavorable effects of the eluting agent on the sorption sites cause a decline in biosorption performance [89]. The low biosorption capacity for biomass regenerated with 0.5 NaOH may be attributed to the presence of electrostatic repulsion between sites of negative charge on the waste C.Vulgaris biomass and the anionic CIP molecules at High pH, further suggesting that the concentrated NaOH was harmful to biomass [90]. The result indicates that CIP loading capacity decreased after regeneration. However, after being treated with 0.1 M sodium hydroxide, the desorbed biomass could be reused without losing little of its biosorption capacity [91].

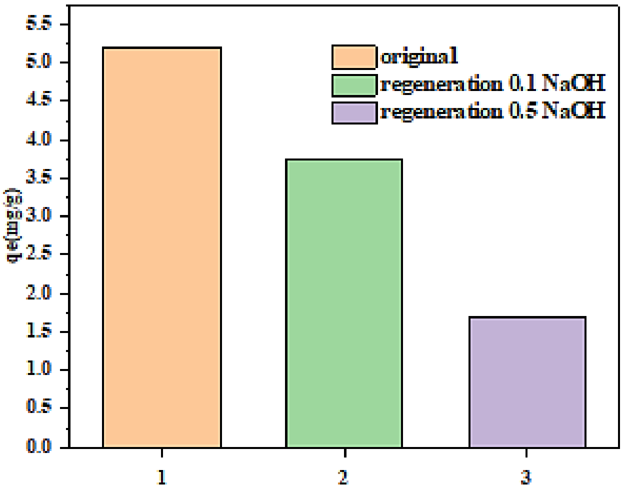


Fig. 7. Cycles of CIP Bisorption for the Extracted C.Vulgaris Biomass and Regeneration Extracted C.Vulgaris by NaOH at Different Concentration (0.1,0.5 M)

5- Conclusions

The study illustrated that the used biosorbent contains a variety of functional groups, according to FTIR analysis, which supports the biosorption mechanism. After the extraction process, the contact area increased, as seen by scanning electron microscopy. The equilibrium data for CIP biosorption onto waste biomass were well fit by the Langmuir isotherm equation, with an R2 of 0.994. The Dubinin-Radushkevich model's free energy value (E = 2.56 kJ mol^{-1}) and the Freundlich model's factor (n=1.59) were used to characterize the underlying physical mechanism, and the exothermic nature of the process is predicted by the Temkin model. The pseudo-second-order model matches the experimental data better, indicating that chemisorption was the preferred rate controller for biosorption. In the regeneration stage, the current study indicates that 0.1 NaOH is more effective than 0.5 NaOH for recovering CIP molecules from the waste of C.Vulgaris biomass. Waste microalgae biomass can be used as an environmentally friendly, efficient, and cheap adsorbent for removing contaminants from wastewater.

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الامتزاز الحيوي للسيبروفلوكسين (CIP) بأستخدام نفايات عملية الاستخلاص من الطحالب الدقيقية: دراسة توازن درجة الحرارة والحركية

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الخلاصة

يدرس العلماء فعالية مختلف المواد المازة لتعزيز الجدوى الاقتصادية والبيئية في تنقية الملوثات. من بين المنتجات الثانوية الاساسية لانتاج وقود الديزل الحيوي هي نفايات الكتلة الحيوية للطحالب الدقيقة، والتي يمكن استخدامها كمادة مازة رخيصة لمعالجة التلوث. في هذة الدراسة ,تم استخدام الكتلة الحيويةالمتبقية بعد عملية الاستخلاص (C.Vulgaris) لاختبار الامتزاز الحيوي المحتمل لسيبروفلوكسين (Ciprofloxacin) من المحاليل المائية المحاكاة. تم تميز قدرة المادة المازة بأستخدام فحوصات FTIR,SEM,EDX. أظهرت تحليل مطياف الاشعة تحت الحمراء أن الامتزاز الحيوي لسيبروفلوكسين حدث بشكل أساسي في المواقع التي تحتوي على مجموعات الكاربوكسيلة والامينية على الكتلة الحيوية. تم تناول بيانات تساوي الحرارة وحركية الامتزاز الحيوي في هذة الدراسة. تتوافق بيانات الامتزاز الحيوي مع نموذج متساوي الحرارة Langmiur مع قدرة امتزاز حيوي قصوى تبلغ ٧,٥٦g/mg ,بينما تم وصف البيانات الحركية للامتزاز الحيوي بدقة بواسطة نموذج الدرجة الثانية. تمت دراسة تجديد مادة الامتزاز الحيوي أيضا باستخدام تركيزين مختلفين من هيدروكسيد الصوديوم ,واظهرت النتائج أنه بعد الامتصاص، انخفضت قدرة الامتزاز الحيوي من ٥,٢ الى ٣,٧٤,١,٧٧ (mg/g) بأستخدام 0.5 NaOH,٠.٠١NaOH . على التوالي.

الكلمات الدالة: الطحالب الدقيقة، بقايا الكتلة الحيوية كلوريلا فلكاريس، الامتزاز، معالجة مياه الصرف الصحي، السيبروفلوكسين.