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Evaluation of Biosorption Potential of Opuntia fragalis Leaf for Decontamination of Cu(II) from Human Blood Plasma: Kinetic and Isotherm Studies

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ABSTRACT

Several heavy metals are found naturally in the earth's crust and are exploited for various industrial and economic purposes. Among these heavy metals, a few have direct or indirect impact in the human body. Some of these heavy metals such as copper, cobalt, iron, nickel, magnesium, molybdenum, chromium, selenium, manganese, and zinc have functional roles which are essential for various diverse physiological and biochemical activities in the body. However, some of these heavy metals in high doses can be harmful to the body and in minute quantities have delirious effects on the body causing acute and chronic toxicities in humans. The process of removal of heavy metals is important due to their toxic effects on living organisms. Conventional methods possess many irreconcilable disadvantages pertaining to cost and efficiency. As a result, an in vitro laboratory-scale batch technique was employed to examine the removal efficacy of a novel unmodified natural biosorbent, Opuntia fragalis leaf (OFL) for detoxification of Cu(II) ions from human blood plasma. The outcome of detoxification of Cu(II) ions from human blood plasma using an unmodified biosorbent was accomplished by optimizing biosorption parameters such as biosorbent dosage, initial Cu(II) ions concentration, pH, and agitation time. The percentage of detoxification increases as the biosorption factors were increased with an optimum biosorbent dose of 2 g, initial Cu(II) ions concentration of 40 mg/L, pH of 6 and contact time of 60 minutes. The unmodified natural biosorbent was characterized to investigate the functional groups responsible for binding the Cu(II) ions from the blood plasma onto the biosorbent using Fourier Transform Infrared Spectroscopy. It was revealed that -N-O, -N-H, -C-C-, and -OH were accountable for Cu(II) ions detoxification from human blood plasma. Scanning electron microscopy (SEM) identified pores present on the biosorbent and revealed the biosorbent's outstanding surface chemistry. The experimental values were subjected to the Langmuir, Freundlich, and Temkin isotherms. The correlation of fitness, R² (0.8231) value of the Langmuir isotherm model correlates best among the biosorption isotherms; thus, it best explains the detoxification process. Q⁰ for Langmuir monolayer coverage is 1.8103 mg/g which infers the maximum amount of Cu(II) ions biosorbed per pore site. The dimensionless factor R_L = 0.0234 implies that the biosorption process is favourable. The Freundlich isotherm biosorption intensity, n is 1.9912 connotes the extent of binding affinity between the Cu (II) ions and the untreated biosorbent. The Temkin isotherm model yielded a biosorption heat of 6.4237 j/mol. In addition, the experimental data were subjected to multiple kinetic models to determine the rate of Cu(II) ions detoxification from human blood plasma. The pseudo-second order model fits best among the examined models, with the highest R² value of 1.

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1- Introduction

Heavy metals are hazardous chemicals prevalent in both natural and anthropogenic environments [1]. These heavy metals are distributed in the environment through several natural processes such as volcanic eruptions, spring waters, erosion, and bacterial activity, and through anthropogenic activities which include fossil fuel combustion, industrial processes, agricultural activities as well as feeding [2]. It also permeates the environment as a result of industrialization and urbanization. It is found in low amounts in natural habitats but at high concentrations in degraded and contaminated habitats, having significant health implications [3]. Contamination with heavy metals contributes to a significant environmental concern due to its negative effects and deposit via the food chain, therefore infiltrating the human body [4]. Heavy metal emissions from agricultural and industrial waste disposal are skyrocketing. These heavy metals do bioaccumulate in living organisms and the human body through various processes causing adverse effects [5]. In the human body, these heavy metals are transported and

compartmentalized into body cells and tissues binding to proteins, nucleic acids destroying these macromolecules and disrupting their cellular functions. As such, heavy metal toxicity can have several consequences in the human body [6]. It can affect the central nervous function leading to mental disorders, damage the blood constituents and may damage the lungs, liver, kidneys, and other vital organs promoting several disease conditions [2,7]. Also, long-term accumulation of heavy metals in the body may result in slowing the progression of physical, muscular, and neurological degenerative processes that mimic certain diseases such as parkinson's and alzheimer's diseases [3,6]. Moreover, repeated long-term contact with some heavy metals or their compounds may even damage nucleic acids, cause mutation, and mimic hormones, and thereby disrupting the endocrine and reproductive system and eventually leading to cancer [8]. Copper is often regarded as one of the heavy metals that endanger the environment [9]. It is one of the most abundant elements in the Earth's crust and its concentrations are rising through human activities [10]. Although it is an essential element for human health as it

from

Dissolved

aqueous

environments

biosorbent biomass should pass through the film

of its surrounding liquid solvent [13]. Biological

materials are organisms like plants, bacteria,

substances on the surface

by

biomass.

of

the

participates in metabolism, stimulates the enzymes and plays an important role in the functioning of immunological system. It becomes toxic at intake levels of 100-500 mg/day [8,9]. Heavy metals such as Cu²⁺, Cd²⁺, Ni²⁺, Pb²⁺, and Zn²⁺ are toxic to human beings and other living organisms if their concentrations exceed threshold values. The most important sources of copper are general industry and mining, plating, fertilizers, paper products, and fibres [11]. When inorganic chemicals like copper are consumed and absorbed, they build in the tissues, but the bones bear 90% of the health load. A high rate of heavy metal exposure affects haemoglobin production, the gastrointestinal tract, the kidney, and the reproductive organs, resulting in severe nervous system impairment. Because of their propensity to dissolve in the avoid hazardous soil and components, biocomposites made of biodegradable polymer and natural fibre have recently gained a lot of attention in the scientific community [12]. Conventional methods for the removal of heavy metals in aqueous solutions include precipitation, flotation, electrodialysis, ion exchange, ultrafiltration, membrane filtration, and adsorption. However, the high costs, operational difficulties, and low removal efficiencies associated with the conventional adsorbents such as activated carbon restrict their large-scale application, especially in developing countries [11]. Natural materials that exist in large quantities or certain waste from agricultural processes may have the potential to be used as low-cost adsorbents, as they represent unused resources, are widely existing and are environment friendly [11,13]. The use of biological molecules rather than physical and chemical methods for the removal of metals from industrial waste is an alternative and very effective method. Applications of biological molecules for the removal of metals include biosorption, adsorption, and phytoremediation methods. Biosorption is the uptake of metal ions

algae, fungi, molds, etc. Besides, during the last years, several biomass twenty sorption characteristics have been examined. Biomass contains various functional groups such as carboxyl, sulfate, phosphate, and amino groups which is responsible for the removal of toxic substances. Among these biomasses, common ones are biomass from microbiological production, wastes from sugar production, crab shell, nuts shells, tea leaf wastes, rice husks, plant materials, etc. [14]. Several methods have been used to detoxify heavy metals, but biosorption, which is the purification or withdrawal of metals or compounds from solution using biological materials, is the most commonly employed. The biosorption mechanism is governed by the adsorbents' origin or source, the biosorbate involved, and the modes of processing. These biosorption methods rely on the interaction of metal ions with functional groups in the process [14,15]. By-products of biomaterial production activities are a cheap source of biosorbents. Several research and experimental studies were conducted about the removal of zinc by adsorption on various biosorbents like carrot residues [15], coffee husks [16], apple wastes [17], cocoa shells18], corn stalks [19], grape pomace [20], potato peels [21], banana peels [22], sawdust and water hyacinth [23], orange waste [24], and olive stone waste [25]. Opuntia fragalis is a Cactaceae plant that is commonly known as a prickly pear. It is nutritious, sweet, and offered as a beverage, as well as therapeutic because its preparation is analgesic, anti-diabetic, anti-inflammatory, and antioxidant thereby making it suitable for the biosorption study [26]. Blood plasma accounts for 60% of total human blood volume. It is composed of the

blood's liquid component and acts as a harmful material transport medium [27]. Water accounts for up to 90% of its makeup, and it also contains coagulation factors, mineral ions, proteins, hormones. carbon dioxide. and glucose biosorbent dosage, pH, and contact time were determined in batch experiments. One of blood plasma's primary jobs is to convey excretory products. As a result, when toxic metals that cannot be metabolized (non-biodegradable) enter the body and are transported by blood plasma, they concentrate in the system, causing health risks to living organisms [8,27]. The present study aims to evaluate the biosorption or detoxification potential of OFL biosorbent for the removal of Cu(II) ions from human blood plasma. Effects of the initial Cu(II) ions concentrations, of the sorbent were predicted with the aid of equilibrium and kinetic models. The interactions of peanut shells with metal ions were analyzed by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. There are several studies about Cu (II) ions removal with different absorbents. But, in the present study, an unmodified natural biosorbent from OFL, which has not been experimented before, was used as an absorbent and Cu (II) ions removal efficiency of the modelled with intermittent system was adsorption isotherm and kinetic models. Sorption experiments were performed in triplicate and the average values of samples were presented. Also, blank samples were used to compare the results through all batch procedures to ensure repeatability and reproducibility.

2. Materials and Methods

2.1. Materials and instruments

The main reagents used in this study are hydrochloric acid (99.9% purity), sodium hydroxide (97.9% purity), copper (II) tetraoxosulphate (VI) pentahydrate (98.9% purity), hydrogen peroxide (99.9%), citrate

phosphate dextrose adenine, human blood plasma, deionized water, and OFL. Beaker, conical flask, measuring cylinder, watch glass, funnel, weighing balance, spatula, stirring rod, sample bottles, mechanical shaker, FTIR spectrophotometer (Germany. Perkin Elmer, USA), Atomic Absorption Spectroscopy (AA240FS Varian), and Scanning Electron Microscope (Hitachi, Japan). All the chemicals used were of analytical grade and required no further purification and treatment. All chemicals were obtained from Sigma Aldrich.

2.2. Methods

2.2.1. Samples collection

The OFL used in the detoxification of Cu(II) ions from human blood plasma were gathered from the garden of Ahmadu Bello University, Nigeria. Human blood samples were obtained in sterile tubes from Ahmadu Bello University Teaching Hospital, Nigeria and subjected to centrifugation and analysis for the presence of heavy metals of concern.

2.2.2. Preparation of Cu(II) ions stock solution

This was prepared by dissolving 3.9291 g of copper (II) tetraoxosulphate (VI) pentahydrate, (CuSO₄.5H₂O) in 200 cm³ of deionised water in a beaker. The beaker content was then quantitatively transferred into a 1000 cm³ flask and diluted to the mark with deionised water. The working solutions were therefore prepared from the standard solution by serial dilution to obtain the required solutions [28].

2.2.3. Preparation of biosorbent for detoxification study

The OFL was rinsed with running water, rewashed with distilled water to eliminate sticky impurities, cut into pieces, and dried for 24 hours at 60 °C. The dried leaves were then crushed in a grinding mill and sieved, with particle sizes ranging from 0.25 to 0.5 mm. Without any pre-treatment, the biomaterial

(OFL) was preserved in a plastic container and used as biosorbent for the detoxification of Cu (II) ions from human blood plasma [28].

2.2.4. Preparation of human blood plasma

To facilitate uniform mixing, the blood was measured into tube containing а an anticoagulant (1.80 mg citrate phosphate dextrose adenine per ml blood). The tube was gently flipped several times to further mix the fluid before being stored at room temperature. After 10 minutes of spinning, three distinct layers were observed: plasma, white blood cells, and red blood cells. The plasma was carefully decanted, and great care was taken not to break the created layers [28].

2.3. Surface characterisation of biosorbent2.3.1. Fourier Transform InfraredSpectroscopy (FT-IR)

The OFL biosorbent was characterized for the presence of functional groups responsible for the adsorption of Cu (II) ions from human plasma using a Perkin Elmer, USA FTIR spectrophotometer. To determine the FT-IR spectra of the biosorbent before and after biosorption, the Perez Meteus et al. [29] method was used. Biosorbent with Cu (II) ions film was prepared by mixing with KBr, the films containing the specimen were inserted into the apparatus, and the infrared spectrum was recorded in the range 400–4000 cm⁻¹. The FT-IR of unloaded biosorbent and biosorbent loaded with Cu (II) ions were compared to determine the functional groups responsible for Cu(II) ions detoxification from human blood plasma.

2.3.2. Scanning Electron Microscope Analysis (SEM)

To investigate the morphology of the OFL biosorbent before and after adsorption and the distribution of the Cu (II) ions onto the biosorbent using an electron microscope (Hitachi, Japan). To obtain microscopic images of the biosorbent, the specimens were bonded to the aluminium substrates using a double-sided adhesive. The aluminium plate was then coated with gold using BAL-TEC SCD 005 coating system (Baltec AG, Balzers, Liechtenstein) and the samples were imaged using Scanning Electron Microscopy [30]. Biosorbent was analyzed for its surface chemistry to ascertain the sites available and responsible for detoxifying of Cu (II) ions from human blood plasma.

2.4. Spiking different concentrations of Cu(II) ions solution into human blood plasma

To assess the degree to which the OFL biosorbent could detoxify Cu(II) ions from human blood plasma, different concentrations of Cu(II) ion solutions were employed to contaminate the human blood plasma [31]. As a result, Equation (1) is presented to compute the volume of Cu(II) ion solution to be added to human blood plasma.

$$V_A = \frac{C_B \times V_B}{C_A} \tag{1}$$

Where, V_A is the volume of spiking solution to be added to the human blood plasma, C_A is the concentration of a spiking stock solution prepared, C_B is the desired spike concentration to be added to the human blood plasma, and V_B volume of the human blood plasma to be spiked.

2.4.1. Batch Detoxification Experiment

The effect of biosorption parameters on Cu(II) ions detoxification was investigated by adjusting the biosorbent dose, Cu(II) ion concentration, pH, and agitation time. The detoxification procedure was performed at physiological temperatures (37 °C). HCl or NaOH was used to change the pH. At a fixed volume of 20 cm³, a known amount of biosorbent was delivered into a solution containing human blood plasma and a spiked concentration of Cu(II) ions, and also stirred by a mechanical shaker to ensure biosorption equilibrium was attained in a suitable period. The mixture was then filtered via filter paper, and the filtrate was evaluated for Cu(II) ion concentrations [32]. The amount of Cu(II) ion detoxified per unit biosorbent is presented in Equation (2). The percentage detoxification of Cu(II) ions from human blood plasma at any time is presented in Equation (3).

$$q_e = \frac{(C_o - C_e)V}{M} \tag{2}$$

Percentage detoxification of Cu(II) ions =
$$\frac{(C_o - C_e) \times 100}{C_o}$$
(3)

Where, M is the biosorbent mass, V is the volume of mixtures, C_o is the initial concentration, and C_e is the final concentrations of Cu(II) ions.

2.4.2. Digestion of Filtrates

A flask was filled with a filtrate containing 1 cm³ of human blood plasma and Cu(II) ion. A mixture of 3 cm³ HNO₃ and H₂O₂ in a 2:1 ratio was added to the filtrate and left to stand for 10 minutes. The flask containing the mixtures was covered with a lid and digested for 1 hour at 6070 °C. In addition, 2 cm³ of HNO₃ and a few drops of H₂O₂ were added to the digest until a transparent digested solution was achieved, while heating at 80 °C was maintained. The surplus acid mixture was heated to semi-dryness before being taken from the hot plate and allowed to cool at room temperature. The digest was transferred to a 100 mL volumetric flask and made up with distilled water to the mark [28].

2.5. Optimisation of detoxification parameters

2.5.1. Optimisation of biosorbent dose

The experiment was carried out in triplicate by weighing diverse biosorbent doses ranging from 0.5 to 2.5 g into different conical flasks hung on a mechanical shaker holding 20 cm³ of human blood plasma and 40 mg/L of Cu(II) ions. The experiment was carried out at a physiological temperature (37 °C) and agitated for 60 minutes. The mixture was then filtered through filter paper, and the filtrates were digested to obtain a clear solution. The digest was analyzed for the presence of Cu(II) ion using Atomic Adsorption Spectroscopy (AAS) [28,33].

2.5.2. Optimisation of Cu(II) ions concentration

The experiment was done in triplicate, different Cu(II) ion concentrations ranging from 10 to 50 mg/L were spiked into different 250 cm³ conical flasks containing 20 cm³ of human blood plasma. The optimized biosorbent dose (2 g) was added to several solutions containing human blood plasma, and the Cu(II) ions were suspended on the mechanical shaker. At a physiological temperature, the solutions were stirred for 60 minutes. After the predetermined time, the filtrates were digested to obtain a clear solution and the digest was analyzed for the presence of Cu(II) ions using Atomic Adsorption Spectroscopy (AAS) [34].

2.5.3. Optimisation of pH

The effect of pH on Cu (II) ions detoxification was examined at the optimum biosorbent dose (2g) and Cu(II) ion concentration (40 mg/L). 20 cm³ of human blood plasma and the optimum concentration of Cu(II) ions were measured three times into various 250 cm³ conical flasks by adjusting the pH of the solutions at 2, 4, 6, 8, and 10 using 0.1 M HCl or NaOH. Before agitation, the optimum biosorbent dose (2g) was put into several flasks suspended on the mechanical shaker. The mixtures were agitated for 60 minutes before being filtered via filter paper. After that, the filtrates were digested and analyzed for the presence of Cu(II) ions using AAS [34].

2.5.4. Optimisation of contact time

The influence of contact time was advantageous in obtaining the required time for the maximum rate of Cu(II) ions detoxification from human blood plasma. The kinetic study was described using the best data. The experiment was carried out by pouring 20 cm³ of human blood plasma into various 250 cm³ conical flasks hung on a mechanical shaker and containing the optimum Cu(II) ion concentration (40 mg/L) and biosorbent dose (2 g) at the optimum pH. (6). The experiment was repeated three times while the mixtures were stirred for 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 minutes. The mixtures were filtered, digested, and then the digests were analyzed for the presence of Cu(II) ions using AAS [35].

3. Results and Discussion

3.1. Fourier Transform Infrared Analysis of biosorbent

Figures 1 and 2 show the biosorbent prior to and after biosorption. The examination of the biosorbent spectra revealed that -C-Br, -C-N, -N-O, -N-H, -C-C-, and -OH were involved in the detoxification of Cu(II) ions. The shift in frequency after biosorption showed that there was a Cu(II) ions binding process at the biosorbent surface. Similar functional groups were reported by [36].



3.2. Scanning Electron Microscope of biosorbent

Figure 3 and 4 demonstrate the SEM results of biosorbent before and after biosorption, respectively. It identified multiple microscopic pores on the biosorbent before biosorption and particle aggregation on the biosorbent's surface after biosorption, demonstrating the ability to detox Cu(II) ions from human plasma [37].



Fig. 3. SEM micrograph of biosorbent before biosorption



Fig. 4. SEM micrograph of biosorbent after biosorption

3.3. Effect of biosorption parameters on Cu(II) ions detoxification3.3.1. Effect of biosorbent dose on detoxification of Cu(II) ions from human plasma

By adjusting the biosorbent dose from 0.5 to 2.5 g, as shown in Figure 5, it was feasible to achieve the requisite percentage of Cu(II) ions detoxification from human plasma onto the biosorbent. It was shown that increasing the biosorbent dose facilitated Cu(II) ions detoxification. This increase could be attributable to the abundance of binding sites and surface area that result in the detoxification of Cu(II) ions from human blood plasma [35]. As the dose of the biosorbent increased, the proportion of Cu(II) ions detoxification reduced. This might be caused by a reduction in the amount of binding surface and biosorbent aggregation, as indicated by the SEM results [34,38].

3.3.2. Effect of concentration on detoxification of Cu (II) ion from human plasma

Figure 6 illustrates the percentage of Cu(II) ions detoxified in relation to human plasma levels. The percentage of detoxification increased from 91.53 to 96.69% when the Cu(II) ions concentration increased from 10 to 40 mg/L. This equivalent increase was made possible by the biosorbent's surface having a large number of vacant sites, which allowed the biosorbent to chelate more Cu(II) ions from human blood plasma [38]. The decrease in the detoxification proportion was probably caused by extra Cu(II) ions vying for vacant sites [35,36].





Fig. 6. Percentage detoxification versus Cu(II) ions concentration with optimal concentration of Cu(II) ions = 40mg/L, pH=6, biosorbent dose = 2 g and agitation time = 60 mins.

3.3.3. Effect of pH on detoxification of Cu(II) ions from human plasma

Figure 7 plots the pH versus the percentage of detoxified Cu(II) ions. The percentage of detoxification increased from 88.89 to 92.83% as pH was raised by 2 to 6. This could be due to low competition between the protons and Cu(II)

ions in the pore sites [39]. pH 6 was obtained as the best pH for detoxifying Cu(II) ions from human blood plasma. However, a decrease from 92.625-90.0725% was observed at pH 10, this could be due to the electrostatic force holding Cu(II) ions, and the biosorbent becomes weakly attracted [34,39].



Fig. 7. Percentage detoxification versus pH with optimal pH=6, concentration of Cu(II) ions = 40 mg/L, biosorbent dose = 2 g, and agitation time = 60 mins at 37 °C

3.3.4. Effect of contact time on detoxification of Cu(II) ions from human blood plasma

Figure 8 depicts the percentage of detoxification of Cu(II) ions versus contact time. It is evident from the results that extending the time improved the percentage of detoxification of Cu(II) ions from human blood plasma by the biosorbent. Cu(II) ions detoxification increased from 93.34 to 97.03% as contact time increased from 10 to 60 mins until equilibrium was attained at 60 mins [28,38]. This increase could be attributed to the prevalence of exposed pores.

Furthermore, equilibrium was reached as remaining pore sites became limited and repulsion between Cu(II) ions and biosorbent occurred. However, [40] observed a comparable equilibrium period for hexavalent chromium removal from an aqueous medium.



Agitation time (min)

Fig. 8. Percentage detoxification versus contact time with optimal Biosorbent dose = 2g, concentration of Cu(II) ions = 40 mg/L, pH = 6, and agitation time = 60 mins

4. Kinetic models

The interaction between reaction rate and reactant concentration is demonstrated by kinetic models [41]. Investigations into the adsorption kinetic model are always recommended because it sheds light on the reaction's mechanism. The mechanism of adsorption process was investigated using the pseudo-first order, pseudo-second order, and Elovich models [29,42].

4.1. Pseudo-first order model

The pseudo-first order is defined in Equation (4).

$$Log (q_e - q_t) = Log q_e - \frac{k_1}{2.303}t$$
 (4)

Where, q_t (mg/g) signifies the proportion of Cu(II) ions detoxified per unit mass of biosorbent at time t, K_1 (L/min) symbolizes the pseudo-first order model's rate constant, t (min) symbolizes the length of time it takes for detoxification to take place, and q_e (mg/g) symbolizes the amount of Cu(II) ion detoxified at equilibrium [43], as presented in Table 1 which demonstrates surplus Cu(II) ions from human blood plasma were speedily detoxified by the biosorbent and Figure 9 with R² plot confirms that detoxification of Cu(II) ions from blood plasma fits pseudo-first order. The K₁ (0.4026 L/min) and q_e (3.30×10¹⁴ mg/g) describe the rate constant and amount of Cu (II) ions detoxified per OFL biosorbent, respectively. This connotes that a large amount Cu (II) ions were detoxified within a short time [41,43]. R² (0.9424) value indicates that detoxification of Cu

(II) ions onto OFL biosorbent fit slightly into the pseudo-first order model when compared with pseudo-second order model due to good correlation between log (qe - qt) and t, as shown in Figure 9 [28].



Fig. 9. Pseudo-first order model of Cu(II) ions detoxification from human blood plasma

4.2. Pseudo-second-order model

The pseudo-second-order kinetic is explained in Equation (5).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Where, q_e is the proportion of Cu(II) ions detoxified per unit mass of biosorbent, qt is the proportion of Cu(II) ions per unit mass of biosorbent at the time, t, and k_2 is the rate constant of the pseudo-first-order (g/mg.mins). Thus, according to Table 1, the pseudo-secondorder model, as shown in Figure 10, adequately describes how Cu(II) ions are detoxified from human blood plasma. This is in contrast to the pseudo-first order and the Elovich model, which both fit R² values more closely. The biosorbent could therefore detoxify harmful Cu(II) ions from human blood plasma within a certain amount of time, as demonstrated by a rate constant, K₂. The q_e (0.3909 mg.g-1) value demonstrates that large amount of Cu(II) ions were removed by OFL biosorbent within limited time, K_2 (3.5143) [43]. R^2 (1.00) connotes that detoxification of Cu(II) ions onto biosorbent follows pseudo-second order model due to good correlation between t/qt and t, as shown in Figure 10 [44].

4.3. Elovich model

The Elovich kinetic model is defined in Equation (6).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$
(6)

Where, β is the desorption constant and α is the original biosorption rate (mg/g.mins) [45]. Table 1 demonstrated, as shown in Figure 11, the use of biosorbent diminished the level of toxicity of Cu(II) ions in human blood plasma. The \mathbb{R}^2 (0.9233)value connotes that detoxification of Cu(II) ions by OFL biosorbent follows the Elovich model thereby defining a chemisorption process, but the process of detoxifying Cu(II) ions from human blood plasma best fits the pseudo-second order (R²=1), the pseudo-second order ($R^2=0.9424$), and Elovich model (0.9233) [44].



Fig. 10. Pseudo-second order model of Cu(II) ions detoxification from human blood plasma



Fig. 11. Elovich model for Cu(II) ions detoxification from human blood plasma

Table 1. Correlation parameter of pseudo-first order, pseudo-second order, and Elovich model

Pseudo-first order				Pseudo-second order			Elovich model		
R ²	q _e (gm/g)	K1 (L/min)	R ²	q _e (mg/g)	K2 ((g/mg.mins)	R ²	A ((mg/g.mins)	B (mg/g)	
0.9424	3.30×10 ¹⁴	-0.4026	1	0.3909	3.5143	0.9233	93.78	0.00748	

5. Equilibrium adsorption isotherm studies

The proportion of biosorbate adsorbed from the solution concentration at a constant temperature is displayed using adsorption isotherms. It describes the biosorbent layers, monolayer types, and biosorbent capacity [44]. Langmuir, Freundlich, and Temkins isotherms were used in this study.

5.1. Langmuir Isotherm

Langmuir model proposed that biosorption happens uniformly on active pores of the biosorbent. The model is best defined in Equation (7).

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^0} \tag{7}$$

Where, q_e is the quantity of Cu(II) ions detoxified per gram of the biosorbent at equilibrium (mg/g), Q^o is the maximum detoxification capacity, K_L is Langmuir constant (L/mg), C_e is the equilibrium concentration of Cu(II) ions (mg/L). Furthermore, essential parameters of the Langmuir isotherm are expressed in R_L which is a dimensionless constant or separation factor presented in Equation (8).

$$R_L = \frac{1}{1 + KlCo} \tag{8}$$

Where, K_L is the energy of biosorption and Co is the initial concentration of Cu(II) ions. The nature of the isotherm is defined by the R_L value. Thus, according to reports, R_L greater than one signifies an unfavorable biosorption isotherm, R_L equals one indicates an isotherm of a linear shape, R_L less than one and R_L equals zero signify favorable and irreversible biosorption а isotherm, respectively [45]. According to Table 2, Q^o (1.8103 mg/g) represents the amount of Cu(II) ions that have been successfully detoxified from human blood plasma, R² (0.8231) represents how poorly the data were correlated, and R_L (0.0234) represents how successfully and favorably the OFL biosorbent detoxified the Cu(II) ions [46].



Fig. 12. Langmuir isotherms of Cu(II) ions detoxification from human blood plasma

5.2. Freundlich Isotherm

The Freundlich isotherm model defines adsorption properties for multilayer surfaces and pore sites with various energies [40]. Equation (9) illustrates the Freundlich Isotherm Equation.

$$Inq_e = InK_f + \left(\frac{1}{n}\right)InC_e \tag{9}$$

Where, C_e (mg/L) is the final concentration of Cu(II) ions, q_e (mg/g) is the proportion of Cu(II)

ions detoxified per unit mass, K_f (L/mg) is the Freundlich constant measuring adsorption capacity, and n is the adsorption intensity. According to Table 2, the K_f (0.9264 mg/g) value illustrated that a significant amount of Cu(II) ions have been detoxified from human blood plasma by the biosorbent with a high biosorption intensity, n (1.9912), and the R² (0.1746) value demonstrated that detoxification capacity of Cu(II) ions from human blood plasma did not fit into the Langmuir isotherm [47].



Fig. 13. Freundlich isotherms for Cu(II) ions detoxification from human blood plasma

5.3. Temkins Isotherm

The Temkins Isotherm is presented in Equation (10).

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$
 (10)

Where, RT/b = B, Ce is the equilibrium concentration of Cu(II) ions, T is the absolute temperature, ${}^{0}K$, and R is the gas constant, q_{e} is the proportion of Cu(II) ions detoxified at equilibrium, and (8.314 J mol⁻¹K⁻¹). In Table 2,

The A_T (6.4237 Lg⁻¹) value explains the interaction between Cu(II) ions and OFL biosorbent is held by low binding energy, b_T (-211.91) value indicates low heat of biosorption [43] and R² (0.3466) shows that Cu(II) ions detoxified from human blood plasma by OFL biosorbent fits the langmuir model best than the Freundlich and Temkins models [42].



Fig. 14. Temkins isotherms of Cu(II) ions detoxification from human blood plasma

Langmuir Isotherm				Freundlich Isotherm			Temkins Isotherm			
R ²	K _L (L/mg)	Q° (mg/g)	RL	R ²	n	K _f (mg/g)	R ²	A _T (L g ⁻¹)	bт (J mol ⁻¹)	
0.8231	1.8099	1.8103	0.0234	0.1746	1.9912	0.9264	0.3466	6.4237	-211.91	

6. Contrast between OFL biosorbent and other biosorbents for Cu(II) ions removal from aqueous or biofluid

To ascertain the biosorption efficacy of OFL biosorbent, it becomes keen to correlate its biosorption parameters and percentage removal with other biosorbents previously mentioned, as shown in Table 3. It is conspicuous that OFL exhibits an outstanding biosorption capacity as a function of biosorption parameters and the maximum percentage removal than other biosorbents. However, the deployment of OFL revealed the biosorption feasibility of Cu(II) ions from human blood plasma. It can be inferred that percentage detoxification of Cu(II) ions from human plasma will be much higher when the OFL is modified.

7- Conclusion

OFL biosorbent was used to detoxify copper from human blood plasma. In this study, OFL is evaluated for its biosorption capacity via a batch process by optimizing the biosorption dose, concentration, pH, and agitation time. The biosorbent was characterized for the presence of functional groups and pore sites using FTIR and SEM, respectively. Its active cogent groups posed as a potent binding site for the removal Cu(II) ions from human blood plasma. The percentage detoxification of Cu(II) ions onto OFL biosorbent raised with increasing biosorbent dose, initial Cu(II) ions pH, and contact time reaching optimum at 2.0 g, 40.0 mg/L, 6.0, and 60.0 mins respectively.

Biosorbent	Biosorbent dose (g)	Concentration (mg/L)	рН	Time (mins)	Max % removal	Ref.
Spirogyra and Cladophora filamentous macroalgae	36.89	57.92	43.24	63.21	79.31	[48]
Cinnamomum camphora leaves	75.82	78.24	69.34	56.45	90.54	[49]
Sugar cane waste	69.09	68.12	68.10	57.34	81.97	[50]
Unmodified Dried persimmon leaves	22.59	47.23	44.37	61.36	73.34	[51]
Pinussylvestris	9.78	37.98	34.92	57.81	73.12	[52]
Opuntia fragalis leaves (OFL)	71.87	83.25	68.36	77.54	97.00	This study

Table 3. Contrast of biosorption capacity of OFL biosorbent with other biosorbent for the removal Cu(II) ions in aqueous and biofluid

The deployment of the Langmuir adsorption isotherm inferred that the biosorption process occurred in a monolayer coverage manner with no interaction between the detoxified Cu(II) ions molecules with each other. The maximum monolayer coverage capacity at 97.0% was 87.54 mg/g. The Freundlich and Temkin models did not show a high accuracy as their correlation coefficients were not as high as the Langmuir isotherm which showed that Langmuir isotherm fits more into the biosorption process with a high correlation coefficient. The pseudo-second order model showed a perfect fit to describe the biosorption process, indicating the chemisorption process. Results showed that OFL demonstrated a suitable biosorbent for the detoxification of toxic metals from biofluids.

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