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Chicken drumstick bones as an efficient biosorbent for copper (II) removal from aqueous solution

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ABSTRACT

The biosorption of copper (II) from aqueous solution on chicken drumstick bones as an efficient biosorbent was investigated. Batch shaking experiments were performed to examine the effects of solution pH (2–7), agitation speed (100–250 rpm), contact time (10–180 min), temperature (25–40°C), biosorbent particle size (250–100 μm), initial metal (50–250 mg L^{-1}) and biosorbent concentrations (2.5–20 g L^{-1}). An agitation speed of 200 rpm was found to be the optimum while the optimum pH was found to occur between a pH of 4–5. The maximum biosorption capacity obtained was 19.08 mg Cu(II)/g adsorbent. Within the range of 25–40°C, the higher temperature was found to boost the biosorption. The results indicate that Langmuir model provides best correlation of experimental data. It is proposed that the copper-uptake process is controlled by surface chemisorption interactions at the earlier stages (0–20 min) and by intraparticle diffusion at the later stages (after 20 min).

Keywords: Bisorption; Copper; Chicken bones; Kinetic models

1. Introduction

The accumulation of heavy metal ions like copper (II) in the aquatic environment is becoming an increasingly significant problem as a result of rapid industrial expansion. Most heavy metals have considerable detrimental effects on the environment as well as the potential to form compounds with toxic, carcinogenic or mutagenic properties. Copper is a broadly used metal with many desirable material properties and variety of applications. As a result, copper (II) ions are one of the more frequently encountered heavy metals in industrial effluents. Although copper is an essential nutrient for humans and other living organisms, it can be highly toxic at high concentrations [1]. Additionally, copper in the environment tends to accumulate in the soil, which can affect plant life and the ecosystem. The combination of the widespread abundance and toxicity of copper (II) ions makes it essential to treat copper bearing effluents before disposal. The World Health Organization recommended a maximum acceptable concentration of copper (II) in drinking water of 1.5 mg/L [2].

Currently, conventional methods for the removal of heavy metals from industrial wastewaters include chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment and evaporative recovery [3]. However, these methods have been found to have various performance limitations, often being inefficient, expensive, or generating large amounts of sludge and other waste products

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that require further disposal. Current research has focused on biosorption, a version of adsorption that involves the binding of metal ions to chemical sites in natural, biological materials, as an alternative method. In the process of biosorption, molecules in solution interact favourably with the surface of a solid material known as biosorbent. An ideal biosorbent material should have a high selectivity, a high capacity, chemical and thermal stability, and a low solubility in the carrier solvents, and be of low cost [4].

The advantages of biosorption over conventional techniques include a high efficiency and selectivity. Biosorbents are also generally of a more environmentally friendly nature, more readily available, and are less expensive. Varieties of potential biosorbents have so far been examined including agricultural waste [1], yeast [3], and activated sludge [5]. Out of all of these, it appears that agricultural waste materials have a high potential as they represent an unused and environmentally compatible resource that can be collected with minimal cost. The capacity of a material to adsorb high levels of heavy metals depends on its surface properties like the chemical composition, surface morphology and wettability [6].

There are four main steps that occur in the process of metal biosorption onto a sorbent surface. Firstly, the metal ions are transported from the bulk phase of the solution to the boundary film around the biosorbent. Next, these ions are transported from the boundary film layer to the physical surface of the biosorbent through external diffusion. In the third step, transport occurs from the surface of the biosorbent into the internal pores through intraparticle diffusion. The final stage is actual uptake of the metal onto the biosorbent surface, through individual or combinations of mechanisms like chemical reactions, physical binding and ion exchange [7]. The slowest of these steps should determine the rate of heavy metal biosorption onto the biosorbent surface.

Chicken bone, the biosorbent of focus, is a low-value by-product of the meat industry, with limited alternative uses. Chicken bones as a biosorbent are sustainable and limitless, non-toxic and environmentally friendly. Being of waste by-product nature will increase the value of chickens and reduce waste disposal and landfill problems. According to the Australian Chicken Meat Federation [8], each person consumes on average 50 kg of chicken per year, resulting in an abundance of animal bone that can be potentially be harnessed for this application. In general, bones are composed of approximately 30% organic and 70% inorganic compounds [9]. The organic phase is mainly protein collagen, while the inorganic phase is mostly cation and anion substituted hydroxyapatite (HAP) with the chemical composition of $Ca_{10}(PO_4)_6(OH)_2$. Both of these phases have the capacity to remove heavy metals from solution. In previous works, it has been proposed that the main mechanism of biosorption for the HAP component is through ion exchange [10].

Several different materials have already been tested for their capacity to adsorb copper ions from synthetic wastewater solutions, Table 1. A study by Al-Asheh et al. [12] is the only previous work found examining the sorption of copper (and nickel) using spent animal bones. The bones used in their experiment originated from a variety of meats as available from the butcher, and the data obtained were limited to examining only the influence of the initial pH, biosorbent concentration and copper concentration. Whether the general animal bone results correlate with the chicken drumstick bone results will be investigated, so the data obtained in the present work could support and further analyse the potential of bone to remove copper from a synthetic aqueous solution.

The aim of this study is to investigate and evaluate the chicken drumstick bones as a potential and efficient biosorbent for heavy metal (copper (II) ions) removal from an aqueous solution. The optimal operating conditions need to be experimentally determined by adjusting the pH, temperature, agitation speed, biosorbent particle size and initial metal and biosorbent concentrations. The biosorption performance of the chicken drumstick bones was mathematically modelled through the Langmuir and Freudlich isotherm equations, in order to assess its potential for a real-world application. The kinetics of the biosorption process also modelled in order to predict the metal pollutant uptake rates. This information is critical for the future design and scale-up of a biosorption treatment.

2. Materials and methods

2.1. Biosorbent preparation

The chicken drumstick bones, used in this study as biosorbent, were appropriately sourced from household environments. The drumsticks were first cooked at 200°C and then the attached meat and fat were cleaned away. The biosorbent was washed thoroughly several times with deionised (DI) water and left to dry in oven at 75°C overnight. The biosorbents were allowed to cool to room temperature, and then grounded finely using a mortar and pestle. The ground biosorbent was then sieved using a 42 (355 μm) mesh to achieve a uniform particle size, and stored in a clean, sealed bag.

Table 1
Biosorption capacity (q) of copper for various biosorbents

Adsorbent	q (mg Cu g^{-1} adsorbent)	Optimum pH	Reference
Apple wastes	10.8	5.5–7	Lee and Yang [11]
Animal bone	135.35	5	Al-Asheh et al. [12]
Birch wood sawdust	4.9	5.5	Grimm et al. [13]
Cotton seed hulls	19.1	–	Marshall & Champagne [14]
Heartwood powder of *Areca catechu*	9.58	5.5	Chakravarty et al. [15]
Pine cone powder	5.76	3–5	Ofomaja et al. [16]
Rubber leaves powder	15.0	4–5	Wan Ngah & Hanafiah [17]
Sour orange residue	21.7	4–6	Khormaei et al. [18]
Tree fern	11.7	–	Ho [19]
Pleurotus cornucopiae	25.25	5	Danış [20]
Waste sugar beet pulp	28.5	4–4.5	Aksu & Isoglu [1]
Wheat shell	10.8	5	Basci et al. [21]
Pretreated *Aspergillusniger* biomass	13.4	5.8–6.0	Mukhopadhyay et al. [22]
Modified wheat shells	17.42	5	Aydın et al. [23]
Olive mill residue	13.5	5	Pagnanelli et al. [24]
Mushroom biomass (*Agaricus bisporus*)	5.59	5	Ertugay and Bayhan [25]
Almond shell	10.53	5	Calero de Hoces et al. [26]
Waste beer yeast	0.51	5	Han et al. [27]
Chicken drumstick bones	19.08	4–5	This study

2.2. Solution preparation

Prior to each experiment, 1 L of a 1,000 mg L^{-1} stock solution of aqueous copper (II) ion was prepared. A 3.938 g of copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) was dissolved in 1 L of DI water and used with the required dilution.

2.3. Biosorption experiments

Firstly, the effect of contact time was investigated at 25°C, agitation speed of 200 rpm, 10 g L^{-1} biosorbent concentration, 355 μm particle size and 100 mg L^{-1} initial Cu solutions. The time to reach equilibrium was determined by sampling at 10, 20, 30, 60, 90, 120, 150 and 180 min intervals. The experiment procedure was repeated at a different initial pH (2, 3, 4, 5, 6 and 7), temperature (25, 30, 35 and 40°C), agitation speed (100, 150, 200 and 250 rpm), particle size (<250 μm, 250–355 μm, 355–425 μm, 425–710 μm and 710–1,000 μm), initial copper concentration (50, 100,150, 200 and 250 mg L^{-1}) and initial biosorbent concentration (2.5, 5, 10, 15 and 20 g L^{-1}) to understand the biosorption mechanism and determine the optimal operating conditions. The biosorption experiments were performed batchwise under different conditions and only one variable was altered at a time; all other variables were kept at the conditions specified.

In a typical experimental procedure, 100 mL of the prepared copper solution was measured into the required number of 250 mL glass screw-cap bottles using a 100 mL measuring cylinder. Then, 1 g of the biosorbent was weighed out and added to each glass screw-cap bottle to get 10 g L^{-1} biosorbent concentration. The pH of the $CuSO_4 \cdot 5H_2O$ salt solution was adjusted using 1 M HCl and 1 M NaOH. The bottles were quickly placed into the incubator shaker (Thermoline Scientific Orbital Shaker Incubator), set at 200 rpm and 25°C ± 1°C. After a specific time period (30, 60, 90, 120, 150 and 180 min), the experiment was stopped and a 50 mL sample from each bottle was centrifuged (A Boeco centrifuge, model C-28A) at 5,000 rpm for 5 min to separate the copper ion solution from the biosorbent. The solution was then filtered, and the AAS was used to determine the final copper (II) ion concentration. The AAS analysis was performed using a Shimadzu flame model AA-7000 spectrometer with a multi-element hallow cathode lamp and an air-acetylene flame. The AAS was set to a wavelength of ~222.6 nm, a slit width of 0.7 nm and an 8 mA current. The AAS was calibrated for every batch of analyses with known copper (II) solution standards. The kinetic experiments were carried out at the determined optimal operating conditions with sampling occurring every 2.5 min, in order to obtain kinetic data.

The main numerical representation of the ability of a biosorbent material to adsorb a particular metal is given by the biosorption capacity, also known as the uptake capacity. For the purposes of this report, the biosorption capacity is defined as a measure of the amount (mg) of copper (II) ions that are adsorbed per unit-weight (g) of biosorbent at equilibrium, and it is calculated according to the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

In this equation, q is the biosorption capacity (mg g^{-1}), C_0 is the initial copper ion concentration (mg L^{-1}), C_e is the equilibrium copper ion concentration (mg L^{-1}), V is the solution volume (L) and m is the dry mass of biosorbent added (g). The higher the biosorption capacity the more efficient the process, as less biosorbent required to remove more copper. The removal efficiency is calculated according to the following equation:

$$\text{Removal efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}$$

3. Results and discussion

3.1. Effect of contact time

Fig. 1 shows the effect of contact time for the biosorption of copper (II) onto drumstick chicken bone. The results indicate that the removal efficiency (amount of heavy metal adsorbed) increases rapidly with the contact time up to 30 min, due to the free binding sites on the drumstick chicken bone. The biosorption approached equilibrium within 40 min as the binding sites on the biosorbent were being used up. Similar conclusion was obtained for different biosorbents [28,29]. After this exponential increase, there is negligible further copper adsorbed from the solution, as the removal efficiency remains fairly constant.

The fast biosorption of drumstick chicken bones could make this material favourable for continuous-flow water treatment system. Bulgariu and Bulgariu [30] suggested green algae waste biomass as a suitable biosorbent for continuous treatment system due to its very fast biosorption.

As the equilibrium time is dependent on the experimental conditions and concentrations, a contact time of 180 min was chosen for the remaining experiments in order to ensure that equilibrium is reached for all variations in experimental conditions.

3.2. Effect of particle size

The particle size of the biosorbent is one experimental parameter that could affect the copper uptake from solution. Previous experiments have shown an increase in the particle size to have both negative and positive effects on the biosorption capacity of certain materials [31]. Therefore, it can be concluded that the overall effect mainly depends on the type of biosorbent and the heavy metal ion tested.

Fig. 2 shows the influence of the chicken drumstick bones particle size on the amount of copper (II) adsorbed from solution. Five different particle size ranges were trialled; <250 μm, 250–355 μm, 355–425 μm,

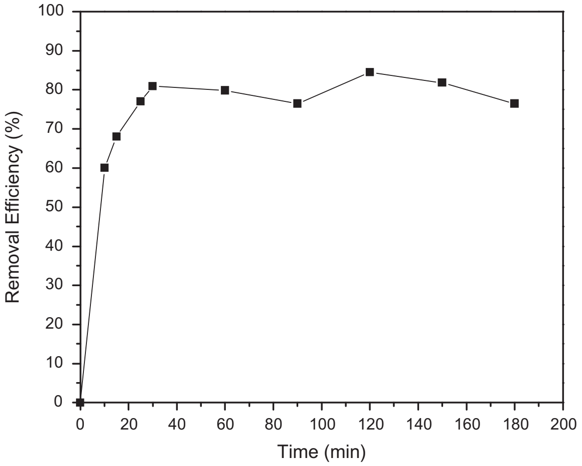

Fig. 1. Effect of contact time for heavy metals biosorption onto drumstick chicken bone (pH 5; biosorbent dose = 10 g L^{-1}, 355 μm particle size, C_0 = 100 mg L^{-1}, Agitation = 200 rpm, T = 25°C).

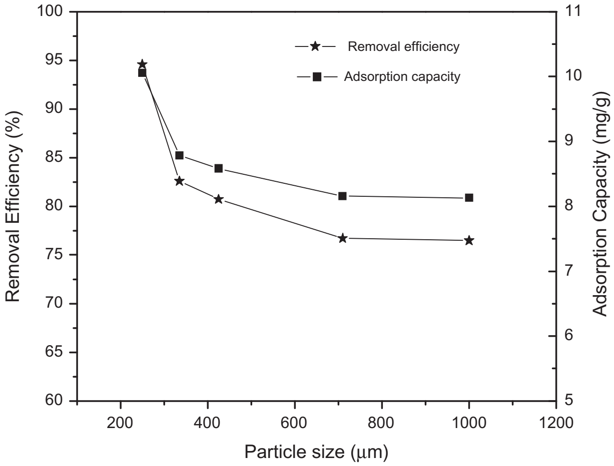

Fig. 2. Effect of the particle size on removal efficiency and biosorption capacity (pH 5; biosorbent dose = 10 g L^{-1}, C_0 = 100 mg L^{-1}, agitation = 200 rpm, contact time = 180 min, T = 25°C).

425–710 µm and 710−1,000 µm. The particle sizes were graphed according to the largest possible particle size in that range. The smallest particle size range of <250 µm removed approximately 24% more copper than the largest particle size range used (710−1,000 µm). From 355 µm and larger, there was a less significant but still apparent decrease in removal efficiency. It is thought that the increase in copper uptake at smaller particle sizes can be attributed to a greater overall surface area, exposing more active binding sites. Additionally, the copper ions have less distance to travel in order to reach the internal surfaces in the pores.

In addition, it was observed that the biosorbent particles began to clump together at larger particle sizes. The clumping of particle further decreases the exposed surface area, and is another potential reason for the lower levels of biosorption at larger particle sizes.

The particle size of the biosorbent highly influences the equilibrium time of biosorption too, although this was not tested. This can provide further information regarding the mechanism of copper biosorption. For example, if biosorption is primarily a surface phenomenon, then a smaller particle size will decrease the time required for transport to the surface and to the internal surfaces of the pore, thus decreasing the diffusional resistance to mass transfer and the time taken to reach equilibrium. Liu et al. [32] investigated the copper ion removal efficiency at different banana peels size and concluded that the fine powder (<150 µm) has the highest removal efficiency (81%) and shortest equilibrium time (1 h). The particle size is an important parameter, affecting the cost of utilising the biosorbent and consequently its feasibility. Smaller particle sizes are harder to achieve, requiring more energy and specialised equipment for grinding purposes.

3.3. Effect of initial solution pH

The pH value may play a determining role with respect to heavy metal ion biosorption according to the related literature [3], as it affects the biosorbent surface charge as well as the degree of ionisation and speciation of the copper ions. The natural pH of the copper sulphate solution was approximately 4.05. Fig. 3 shows the maximum removal of copper occurring between a pH of 4–5. At the lower pH values, less copper was adsorbed from solution. This can be attributed to the abundance of H^+ ions in solution that compete with and inhibit the binding of the copper ions. These positively charged hydrogen ions surround the biosorbent surface, repelling away the positively charged copper ions. Additionally, they occupy the binding sites of the chicken bone biosorbent competing with the copper ions for biosorption.

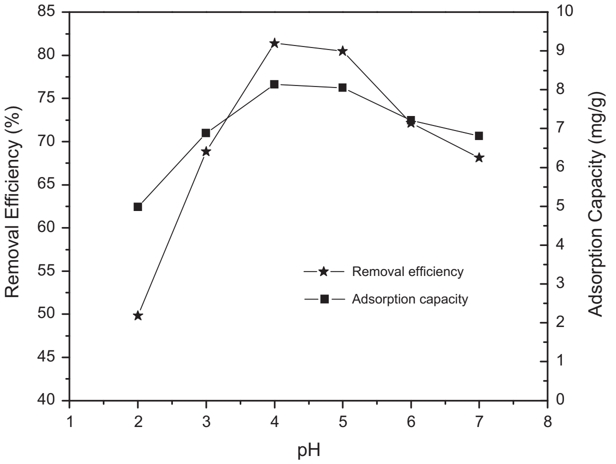

Fig. 3. Effect of the pH on removal efficiency and biosorption capacity (biosorbent dose = $10\,g\,L^{-1}$, $C_0 = 100\,mg\,L^{-1}$, agitation = 200 rpm, contact time = 180 min).

At a pH of above 5, it is through that the copper has precipitated out of solution in the form of the insoluble copper complex, $Cu(OH)_2$, and therefore is no longer available for biosorption. At these higher pH values, more OH^- ions are concentrated in the solution and this complex is more likely to form [3]. At a pH of 6 and 7, the copper sulphate solution was visibly blue in colour, further supporting this claim. Therefore, the pH must be kept at 4–5.

It would be beneficial to determine the point of charge of the biosorbent surface in order to be able to determine the surface charge of the chicken drumstick bone so as to further discuss the interactions influence of the pH on surface attachment. Many other works using various biosorbents for the removal of copper ions from solution have also found the optimal pH values to occur around pH values of 4 and 5, as demonstrated in Table 1. Al-Asheh et al. [12] suggest that soft ions such as Ca^{2+} and K^+ are more favourably released and replaced by copper (II) around a pH of 5. The Ca^{2+} ions originate from the HAP, the major constituent of bones. The coinciding of the optimal pH range with this value supports their theory that ion exchange is the mechanism of biosorption for copper onto chicken drumstick bones.

3.4. Effect of temperature on biosorption

The results of the temperature effects on the biosorption of copper (II) from aqueous solution investigated at 25, 30, 35 and 40°C are shown in Table 2. An increase in temperature up to the selected 40°C range has a positive effect on the amount of copper adsorbed onto the chicken bone surface. At 40°C, the removal

Table 2
Temperature variation data

Temperature (°C)	Removal efficiency (%)	q (mg g^{-1})
25	79.7082	7.97082
30	79.8983	7.98983
35	82.2344	8.22344
40	86.4764	8.64764

efficiency and the biosorption capacity of copper (II) were 86.47% and 8.65 mg g^{-1} respectively. As the temperature is increased, the kinetic energy of the molecules in the system becomes higher. The copper ions and the biosorbent particles are moving more rapidly, at faster velocities, and the likelihood of collision between these groups is increased. Ratnakumari and Sobha [29] found that the biosorption of copper (II) by the chick and duck feathers was rapid up to 40°C and later decreased with increased temperature. The percentages of the removal of copper by chick and duck feathers were 80.7 and 78.83% respectively.

In some works, an increasing temperature has been found to decrease the removal efficiency [1]. In these instances, it is thought that deactivation of the biosorbent surface begins to occur as the active sites are destroyed, and the surface bonds are not able to be maintained at these high energies. The temperature at which this phenomenon would begin to occur for this system is presumably above the measured temperature range. It is recommended that higher temperatures ranges be studied to investigate this further.

3.5. Effect of agitation speed on biosorption

Agitation is an essential component of biosorption as it ensures a uniform solution and promotes effective mass transfer. These effects maximise the potential for contact between the copper ions in solution and the appropriate binding sites on the surface of the biosorbent. Additionally, agitation can decrease the film resistance associated with a stationary fluid, which is a barrier to mass transfer [33].

Agitation speeds of 100, 150, 200 and 250 rpm were tested and the optimum agitation speed was found to be 200 rpm according to Fig. 4. At lower agitation speeds, there is less contact between the copper ions and biosorbent surface. As a result, mass transfer is limited and the removal efficiency is lower. As the agitation speed is increased, the potential for contact is increased as the rate of diffusion of copper ions to the surface increases. Thus, the mass transfer resistance is lower and more copper is adsorbed. The biosorbent molecules are also less clumped together, increasing the total accessible surface area for biosorption.

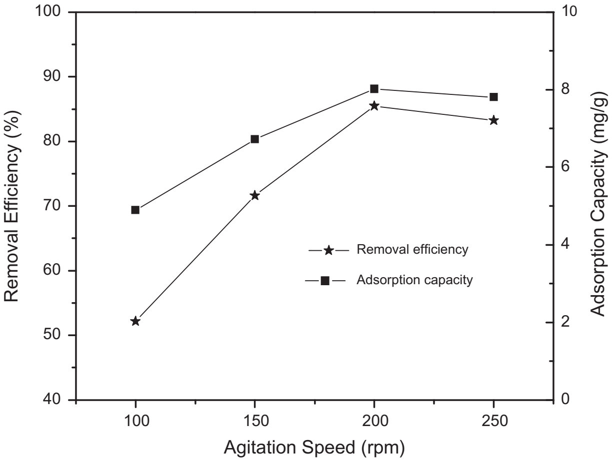

Fig. 4. Effect of the agitation speed on removal efficiency and biosorption capacity (pH 5; biosorbent dose = 10 g L^{-1}, contact time = 180 min, C_0 = 100 mg L^{-1}).

The amount of copper removed from solution slightly decreased when the agitation speed was set to the maximum 250 rpm. This may be attributed to the increase in energy causing the newly formed bonds between the biosorbent and sorbate to break. The occurrence of an optimal agitation speed is also observed in experiments by Parvathi et al. [33] and Saikaew and Kaewsarn [34] for the biosorption of lead and cadmium ions, respectively.

3.6. Effect of biosorbent dose on biosorption

The removal efficiency of copper ions at different dose of chicken bone biosorbent is shown in Fig. 5. At the standard experimental conditions, 0.25, 0.5, 1.0, 1.5 and 2.0 g of biosorbent were added to 100 ml of 100 mg L^{-1} copper solution. As the dose of biosorbent is increased, there is initially a considerable increase in removal efficiency that is followed by a slower approach to complete removal of copper, which occurs at a mass of 2 g.

Increasing the ratio of biosorbent to copper ions in solution increases the removal efficiency because it provides a larger total surface area and more potential binding sites for biosorption. However, with a higher dosage of biomass, the biosorption capacity is affected in a different manner. The maximum biosorption capacity is observed at an adsorbent dose of 0.5 g. At a lower dosage, the adsorbent is fully saturated and not able to adsorb any more copper. At higher doses, although the total amount of copper removed from solution increases, the overall process becomes less

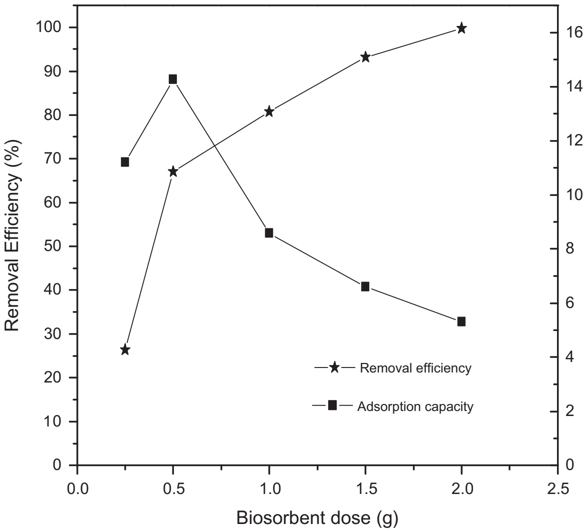

Fig. 5. Effect of the biosorbent dose on removal efficiency and biosorption capacity (pH 5, contact time = 180 min, $C_0 = 100\,\mathrm{mg\,L^{-1}}$, agitation = 200 rpm, $T = 25°\mathrm{C}$).

efficient as there is a lower driving force for copper biosorption onto the biosorbent surface. This biosorption capacity curve for different biosorbent doses is very similar to those obtained by Tumin et al. [35] for the biosorption of copper using *Elais Guineensis* kernel activated carbon.

3.7. Effect of initial copper concentration on biosorption

The effect of the initial copper concentration in solution on the removal efficiency was examined with 50, 100, 150, 200, and 250 $\mathrm{mg\,L^{-1}}$ concentrations. The results in Fig. 6 demonstrate a decrease in the amount of copper adsorbed from solution with an increase in the initial copper concentration. At low concentrations, there is a greater ratio of binding sites to copper ions, which means that likelihood of these ions finding active and available binding sites on the biosorbent surface is larger. At higher initial copper concentrations, more copper ions are left unadsorbed at equilibrium as the biosorbent binding sites become saturated.

However, at higher initial copper concentrations, more copper is adsorbed per mass of biosorbent as shown by the biosorption capacity. The higher copper concentrations provide a driving force to overcome mass transfer resistance [1], as energetically less favourable binding sites become involved. Copper ions have a higher affinity towards the active sites and the probability of collision between the biosorbent and metal ions is also larger. Thus, the biosorption capacity is increased with increasing copper concentration. According to Goksungur et al. [3], a higher metal ion concentration also extends the time taken to reach equilibrium.

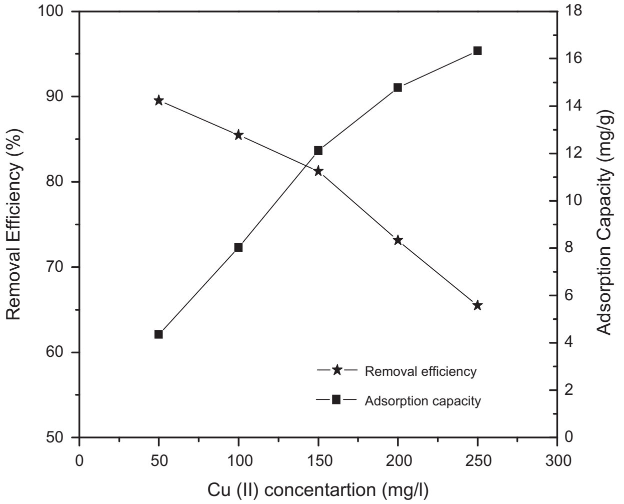

Fig. 6. Effect of copper concentration on removal efficiency and biosorption capacity (pH 5, contact time = 180 min, biosorbent dose = 10 $\mathrm{g\,L^{-1}}$, agitation = 200 rpm, $T = 25°\mathrm{C}$).

According to the above conclusions, it is recommended that wastewaters are diluted before processing in order to obtain the maximum recovery of copper ions from industrial effluents.

3.8. Biosorption isotherm modelling

Biosorption isotherms are used to describe the amount of metal adsorbed as a function of the equilibrium metal concentration, at a constant temperature. The quantity adsorbed is normalised against the mass of adsorbent, to allow for a comparable data. The experimental data obtained in the previous section for the different copper concentrations was fitted to both the Langmuir and Freundlich models; two of the most frequently applied isotherm models. The Langmuir isotherm model is described according to the following equation:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{3}$$

where q_e represents the equilibrium metal ion concentration on the adsorbent ($\mathrm{mg\,g^{-1}}$) and C_e is the equilibrium metal ion concentration in solution (mg $\mathrm{L^{-1}}$). q_m and b are constants, where the former represents the monolayer capacity of the adsorbent ($\mathrm{mg\,g^{-1}}$) and the latter indicates the sorbent affinity at low concentrations (mg $\mathrm{L^{-1}}$), according to Zhang et al. [36]. The Langmuir isotherm is based on a strict set of assumptions. It assumes the biosorption of an ideal fluid onto an ideal uniform surface where all sites on the adsorbent surface are equivalent. It also assumes that each site can only hold one molecule of adsorbate and that there are no interactions between the adsorbate molecules on the surface. In order to fit the experimental data and obtain the Langmuir constants, the preliminary Langmuir equation is converted into its linear form, as follows:

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

A strong linear correlation represented by the linearised form of the Langmuir equation was obtained and the estimated constant parameters are tabulated in Table 3.

The Freudlich isotherm provides another method for modelling the biosorption. Like the Langmuir equation, it also assumes a monolayer biosorption. However, it considers the surface roughness, or a homogeneous surface, as well as adsorbate interactions. The Freudlich isotherm is provided according to the following equation.

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F is a constant relating to the biosorption capacity while n is a constant relating to the biosorption intensity. Again, it is converted to its linear form for the purpose of modelling, in order to obtain the Freudlich constants.

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \tag{6}$$

The estimated constant parameters are also tabulated in Table 3. Table 3 shows that both isotherm models fitted the data well, but that the Langmuir isotherm was a better fit. This means that the Langmuir model, with the calculated constants, can be used with a high level of confidence to predict the amount of metal adsorbed as a function of the equilibrium metal concentration, at a constant temperature of 40°C.

The Freudlich constants for the sorption of copper from chicken drumstick bones can be compared to those obtained by Al-Asheh et al. [12] for copper sorption using spent animal bones. At a pH of 4, they found that $K_F = 2.127$ and $n = 0.9690$. The K_F value is comparable to that achieved in this work, but the n value did not compare as closely. The higher n value achieved in the present work suggests that the energy of biosorption, or binding energy, is greater for chicken drumstick bones than the general combination of various animal bones used in the other work. This may also be an explanation for why the cited work achieved a significantly higher biosorption capacity.

Table 3
Isotherm model parameters and correlation coefficients

Isotherm model	Parameters	R^2 coefficient
Langmuir	$q_m = 19.9203, b = 0.04744$	0.99
Freudlich	$K_F = 2.0322, n = 2.1124$	0.96

3.9. Kinetic modelling

The kinetics of biosorption provides the rate of uptake of the copper ions onto the chicken drumstick bone particle surface and, consequently, affects the equilibrium time. Kinetic modelling of the biosorption process can be used to determine the uptake of copper (II) mechanism of the chicken bone biosorbent. For this modelling, the biosorption process is modelled according to a synthetic reaction on the surface of the sorbent. The most frequently considered kinetic models for biosorption include the pseudo-first-order equation, the pseudo-second-order equation, the Elovich equation and the intraparticle diffusion equation [37]. Pseudo-first-order, pseudo-second-order, and Elovich equations consider the whole biosorption process, while the intraparticle diffusion equation suggests intraparticle diffusion as the rate-determining step. Therefore, the model that best fits the kinetic biosorption data provides insight into how the biosorption takes place.

The final experiment was run for 40 min with samples being taken every 2.5 min. The selected experimental conditions included an agitation speed of 200 rpm, temperature of 40°C, pH of 4, 250 μm particle size, a copper concentration of 250 mg L^{-1} and a biosorbent dose of 0.5 g. The rate of uptake appears to be fairly consistent, up until a time of 27.5 min, when equilibrium has been reached, Fig. 7. At this time, the biosorption capacity is at approximately 19.08 mg g^{-1}. This does not correlate well with the 135.35 mg g^{-1} biosorption capacity obtained by Al-Asheh et al. [12] for spent animal bones. Reasons for this large difference could be attributed to the experimental conditions, and the type of bone used.

The above-mentioned kinetic equations were used to model the rate of biosorption. The constants from each equation are tabulated in Table 4. The pseudo-first-order equation is shown in equation 7 where q_e is the equilibrium biosorption capacity (mg of copper adsorbed per g of biosorbent), q_t is the biosorption capacity (mg of copper adsorbed per g of biosorbent) at a time t (minutes) and k_1 is the rate constant (min^{-1}):

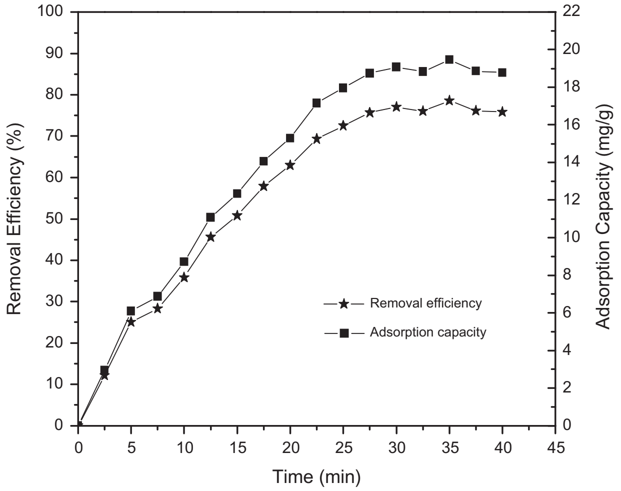

Fig. 7. Typical experiment run for biosorption kinetic study (agitation speed= 200 rpm, temperature = 40°C, pH = 4, 250μm particle size, $C_o = 250\,\mathrm{mg\,L^{-1}}$, and biosorbent dose = $5\,\mathrm{g\,L^{-1}}$).

Table 4
Correlation coefficients and parameters for the kinetic rate equations

Kinetic equation	Parameters	R^2 coefficient
Pseudo-1st order	$k_1 = 0.18562$, $q_e = 21.0647$	0.97
Pseudo-2nd order	$k_2 = 0.0004347$, $q_e = 32.573$	0.94
Elovich	$\alpha = 7.2886$, $\beta = 95.404$	0.92
Intraparticle diffusion	$k_3 = 0.2226$, $C = 1.0505$	0.99

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{7}$$

This equation can be integrated assuming the boundary conditions of $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, into the linear form as follows:

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_t t}{2.303} \tag{8}$$

Plotting $\ln(q_e - q_t)$ against t shows a strong correlation of 0.97 up until a time of 20 min. Any data after this time showed little correlation, so results were only plotted up to a time of 20 min. The short-term application of the pseudo-first-order model is consistent with many literatures, where it has been found to apply only up until a time of 20–30 min [38,39].

If the pseudo-first-order equation is obeyed, the y-intercept of the plot should be equal to $\ln(q_e)$. For the data obtained, $\ln(q_e) = \ln(19.084) = 2.95$, which is very close to the y-intercept that occurs just above 3. The calculated q_e from the model was 21.06, which is similar to the actual q_e of ~19.084. From this, it can be concluded that this model is a strong fit-up until a time of 20 min.

The pseudo-second-order equation is given according to the equation:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

The rate constant k_2 has the units of ($\mathrm{g\,mg^{-1}\,min^{-1}}$). This equation can also be integrated assuming the same boundary conditions of $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, into the linear form of:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

Plotting t/q_t against t gives a linear relationship with a correlation coefficient of 0.94 which is lower than that of the pseudo-first order equation, however, the model applies over the whole range of data. Nonetheless, the q_e calculated through this model of 32.57 is much higher than the actual q_e of 19.084, and so this model is not an accurate representation of the rate of biosorption of copper onto the chicken drumstick biosorbent.

The Elovich equation is written as follows:

$$\frac{dq}{dt} = \alpha \exp(-\beta q) \tag{11}$$

α and β are constants, where the former is a measure of the initial sorption rate ($\mathrm{mg\,g^{-1}\,min^{-1}}$) and the latter is a measure of the extent of surface coverage of the metal ion on the biosorbent ($\mathrm{g\,mg^{-1}}$). This equation can be integrated and rearranged with the same boundary conditions into the following linear form:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t) \tag{12}$$

A plot of q_t against $\ln(t)$ shows the weakest correlation of all the examined kinetic models.

The final kinetic model based on intraparticle diffusion is given as follows:

$$q_t = k_3 t^{0.5} + C \tag{13}$$

k_3, the rate constant for this equation, has the units ($\mathrm{mg\,g^{-1}\ min^{-1/2}}$) and the constant C is a representation of the boundary layer thickness ($\mathrm{mg\ g^{-1}}$). A plot of $t^{0.5}$ against q_t shows a very strong linear correlation of the data producing a correlation coefficient of 0.99. However, the line of best fit does not pass through the origin, which is a requirement if this model is to be obeyed. The strong linear correlation indicates that intraparticle diffusion is involved in the sorption process, but the non-zero intercept suggests that it is not the rate-controlling step [40].

Table 4 compares the correlation coefficients of the various kinetic rate equations (Eqs. (8), (10), (12) and 13). It can be seen that the pseudo-first-order and intraparticle diffusion equations have the highest correlation coefficients. It is believed that the biosorption process for copper onto the chicken drumstick bones is a two-stage combination of surface sorption and intraparticle diffusion.

As mentioned, the pseudo-first-order model is shown to be valid only up until a time of 20 min and not in the latter stages. On the other hand, the intraparticle diffusion plot shows a larger scatter of data within the initial 10 min and a stronger correlation following that. Additionally, the line of best fit does not pass through the origin as would be expected if intraparticle diffusion were the main biosorption mechanism. From this, it is proposed that the copper-uptake process is controlled by surface chemisorption interactions at the earlier stages (from 0 to between 10–20 min) and by intraparticle diffusion at the later stages (after 10–20 min), once the surface sites are saturated and the copper particles have had a chance to diffuse into the inner pores. This confers with the conclusions of Kumar et al. [41], for the biosorption onto press mud.

4. Conclusions

The results of this steady indicate that the chicken drumstick bone can be used as a promising biosorbent for the removal of copper (II) from an aqueous solution. The maximum biosorption capacity was achieved at pH 4–5, smaller particle sizes (<250 μm), and 40°C. The higher temperatures were found to boost the biosorption capacity. The kinetic results correlated well with pseudo-first-order and intraparticle diffusion kinetic equations. It is proposed that the copper-uptake process is controlled by surface chemisorption interactions at the earlier stages and by intraparticle diffusion at the later stages (after 20 min).

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