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# EQUILIBRIUM MODELING OF Cu (II) BIOSORPTION ONTO UNTREATED AND TREATED FOREST MACRO-FUNGUS *FOMES FASCIATUS*

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**ABSTRACT:** Discharge of heavy metal laden wastewaters into the aquatic environment continues to inspire research into the development of low-cost treatment technologies. The identification of low-cost biosorbents and their subsequent optimization particularly through surface modification has been reported to improve the efficiency of biosorption process. This study investigates the biosorptive performance of treated and untreated forest macro-fungus *Fomes fasciatus* for the uptake of Cu (II) ions (a model cation) from aqueous solution. Batch equilibrium experiments at room temperature were conducted to assess removal as a function of solution concentration and biosorbent mass. An improvement of 17.5 per cent increase in sorption capacity as well as an accompanying increase in affinity was observed as a result of hot-alkali treatment of the biosorbent. Primary equilibrium data was analyzed by linear and non-linear regression using the Langmuir and Freundlich two-parameter models as well as the Redlich-Peterson and Sips three-parameter models. The goodness of fit was assessed using the coefficient of determination, $r^2$, the Relative Percent Error, RPE, Marquardt's Percent Standard Deviation, MPSD and Hybrid Error Function, HYBRID. The two-parameter Langmuir model exhibited a high correlation to the experimental data and was successful in providing some insight into the biosorptive process. The three-parameter models produced the highest correlation to the equilibrium data, sufficient to enable the future development of predictive models.

**Keywords:** Biosorption; Equilibrium Isotherm, Langmuir, Freundlich, Redlich-Peterson, Sips, Alkali Treatment, Forest Macro-Fungus

## INTRODUCTION

The term heavy metal has come to embrace any metal, exposure to which is clinically undesirable and which constitutes a potential hazard [2]. The occurrence of heavy metal pollution in the aquatic environment remains a threat to human health, our ecosystem as well as disrupts aerobic and anaerobic treatment systems. This is due to the cumulative and toxic nature of some heavy metals even at low limits. Available technologies for removal of heavy metals from waste streams such as ion exchange, chemical precipitation and adsorption using activated carbon are often viewed by small industries as uneconomical and a financially burdensome option [25]. As such, the screening, optimization and design of biosorption technologies using low-cost, abundantly available, natural heterogeneous materials continue to gain considerable momentum. The cost of cultivating biomass for biosorption can vary from 1-5 $/kg while activated carbon and ion exchange resins varies from 2-5.5 $/kg and 13-30 $/kg respectively [4]. As such, biosorption not only can replace conventional treatment systems but may also be incorporated alongside as polishing units [4].

Fruiting bodies of macro-fungus are considered well suited for biosorption due to the high biosorptive potential exhibited by many fungal species [15]. Optimization of the biosorption process can be realized through varying solution parameters as well as surface modification of the biosorbent. Surface modification has been reported to improve the overall sorption capacity, improve use and reuse of the biosorbents as well as improve the affinity for specific contaminants. The biosorption process involves mainly cell surface sequestration, thus cell wall modification through physical (heating) and chemical (acid and alkali) treatment can greatly alter the binding of metal ions [7]. Such treatment has been successfully applied to fungal biosorbents as *Fusarium solani* [3], *Aspergillus niger* [11] and *Penicillium lanosa-coeruleum* [9]. Dead macro-fungus *Ganoderma lucidum* was found to exhibit a significant increase in metal binding following hot-alkali treatment [14].

Equilibrium isotherms are of fundamental importance in the assessment of biosorbent performance and the design of biosorption systems. This analysis provides an indication of sorption capacity, sorption mechanism, as well as, gives some insight into the affinity of the biosorbent for the metal ion species. An accurate mathematical description of the equilibrium isotherm is also essential to the effective design of sorption systems [8]. Existing isotherm models originally developed for gas adsorption on surfaces have been successful used in modeling biosorption from aqueous solution unto complex biological surfaces. However such applications should be limited to the mathematical representation of the data and mechanistic inferences should be drawn carefully [27].

In this investigation, the effect of hot-alkali treatment on the biosorptive performance of *Fomes fasciatus* is reported. Equilibrium simulation of the biosorption process is examined using the two-parameter Langmuir and Freundlich models as well as the three-parameter Redlich-Peterson and Sips models. Sorption processes were modeled in an attempt to get an insight into the biosorptive process and to select an appropriate equilibrium model that can aid in the eventual development of predictive models to enable process design of batch treatment systems with minimal experimentation.

## MATERIALS AND METHODS

### Sampling and Identification of Biosorbent

Biosorption studies were carried out in batch reactors using a wood rotting macro-fungus found growing in the central range forest of Trinidad. This macro-fungus, which is not used in Trinidad and Tobago (WI) as a commercially viable mushroom, was found growing on dead tree trunks. Collected samples were subsequently identified with the assistance of the Royal Botanical Gardens, Kew, UK, and the Herbarium at the University of the West Indies, Trinidad to be *Fomes fasciatus* (Swartz : Fries) Cooke, belonging to the order Polyporales and family Polyporaceae.

### Preparation of Biosorbent

The handpicked macro-fungus specimens were dried at 90 $^0$C for 1 hour, and then pulverized in a mortar and pestle. They were subsequently washed in distilled water and sieved to a particle geometric mean size, (GMS) of 0.5 mm. Pretreatment of the biosorbents was conducted using a method reported in the literature [16]. Forty (40) grams of the biosorbent was treated with 100 ml of 40 per cent NaOH at 128 $^0$C for 4 hours. The residue was separated, washed with distilled water and then dried at 40 $^0$C for 24 h.

### Analytical Methods

Batch experiments were conducted using Cu (II) as a model cation. Copper stock solution was prepared from copper sulphate in distilled water and estimated by the Cuprethol method (APHA, 1971). The intensity of the coloured complex formed was measured at a wavelength of 435 nm using an ultraviolet spectrophotometer (Milton Roy – Spectronic 601). The determination of copper was verified periodically using an Atomic Adsorption Spectrophotometer, (Perkin-Elmer 3030B). A constant pH of 5.5 was maintained throughout the reaction by a 0.01M acetate buffer and measured using a pH meter (Accumet Research-AR10, Fisher Scientific). Conductivity of the reaction solution was measured using a conductance bridge (YSI Model 31A).

## Equilibrium Biosorption Studies

Equilibrium biosorption studies were carried out in triplicate (the variation was found to be within 5%) using batch reactors at room temperature (26 ± 2 $^0$C). The reaction mixture was spiked with varying concentrations of synthetic Cu (II) solutions and varying adsorbent doses in 100 ml conical flasks. Sorbent masses were accurate to ±0.001 g and solution volumes to ±0.5 ml. The study was carried using initial Cu (II) concentrations varying from10 mg/l to 100 mg/l and adsorbent masses varied from 500 mg/l to 4000 mg/l. The reaction mixtures were agitated in a mechanical shaker at 200 rpm for 60 minutes, which was previously determined by kinetic studies as the time to reach equilibrium. The biosorbent, *Fomes fasciatus*, was then separated by gravity filtration using qualitative filter paper. The filtrate was subsequently tested for residual metal ions. A blank comprising distilled water and *Fomes fasciatus* was prepared to monitor and control any interference due to leaching during the test period. To determine the optimum pH, the reactor was influenced by the addition of appropriate amounts of HCl and NaOH to achieve pH within the range of 2.5 to 10. Maximum biosorption was observed to occur at pH 5.5. The amount of Cu (II) ion adsorbed per unit mass of adsorbent was obtained using the equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where $q_e$ (mg/mg) is the mass of adsorbate sorbed per mass of biosorbent, $C_0$ (mg/l) is the initial concentration of metal ions in solution, $C_e$ (mg/l) is the final concentration of metal ion in solution, $V$ (l) is the volume metal ion solution and $m$ (mg) is the mass of adsorbent.

## Two-Parameter Isotherm Models

The most popular reported isotherm models are the Langmuir and Freundlich equations. In 1916, Irvin Langmuir developed a theoretical equilibrium isotherm relating the amount of gas adsorbed on a surface to the pressure of the gas. The Langmuir isotherm is based on the assumption that points of valency on the surface of the adsorbent have equal affinity for molecules and is capable of adsorbing one molecule; thus, the adsorbed layer will be one molecule thick. The equation can be arranged into the four (4) linear forms, which are presented in Table 1 [22]. In 1906, Freundlich developed an empirical equation, which is a special case for sorption unto heterogeneous surfaces [6]. This equation along with its linear form is also presented in Table 1.

## Three-Parameter Isotherm Models

The Redlich-Peterson [20] and Sips [8] three-parameter model both incorporates the features of the Langmuir as well as the Freundlich isotherms. These models are presented in Table 2.

## Separation Factor

Using equation (9) the separation factor is determined [28]. The nature of the sorption process is further categorized in accordance with Table 3.

$$R_L = \frac{1}{1 + K_L C_e} \tag{9}$$

where $C_e$ (mg/l) is the final concentration of metal ion in solution and $K_L$ (l/mg) is the Langmuir constant related to the free energy of sorption.

## Specific Surface Area

The specific surface area, *S*, was calculated using equation (10) and the monolayer coverage of the biosorbent surface by Cu(II) ions [17].

$$S = \frac{q_m NA}{M} \tag{10}$$

where *S* is the specific surface area, ($m^2$ per g of biosorbent); $q_m$ the monolayer sorption capacity, (g Cu (II) ions per g biosorbent); *N* the Avogado number, ($6.02 \times 10^{23}$ /mol); *A* the cross-sectional area of the Cu (II) ion, ($m^2$); *M* the molecular weight of Cu (II) ion, (g/mol*)*.

### Error Analysis

The goodness of fit of the various kinetic models to the experimental data was evaluated using linear coefficient of determination, $r^2$ as well as the relative percent error, RPE [21], Marquardt's Percent Standard Deviation, MPSD and Hybrid Error Function, HYBRID [22] which are presented in Table 4.

## RESULTS AND DISCUSSION

Sorption isotherms are important to explain how solute interacts with sorbent and it is critical in optimizing the use of sorbents [26]. Specifically, they aid in the development of predictive models enabling process design; determine whether a biosorbent can attain a particular treatment limit; provide a basis for comparison of among various biosorbents; and aid in estimating the performance of full-scale batch and column systems. In the present study, the biosorptive performance of untreated and chemically treated *Fomes fasciatus* was investigated as a function of initial Cu (II) concentration and biosorbent mass.

## Equilibrium Analysis using Two-Parameter Models

The applicability of the Langmuir isotherm to simulate untreated and treated *Fomes fasciatus* uptake of Cu (II) was analysed. The Langmuir equation yields the constants $q_m$, (mg/mg) the maximum sorption capacity, and $K_L$ (l/mg) the constant related to the free energy of sorption. The simplest method to determine isotherm constants is to transform the isotherm variables so that the equation is converted to a linear form and then to apply linear regression [12]. The four (4) linearized forms of the Langmuir model viz. equations (2) to (5), were first applied to the primary equilibrium data. The model parameters presented in Table 5 were obtained by linear plots of ($C_e/q_e$ vs. $C_e$), ($1/q_e$vs. $1/C_e$), ($q_e$ vs. $q_e/C_e$) and ($q_e/C_e$ vs. $q_e$) [22]. The coefficient of determination also presented in Table 5, was used to assess the goodness if fit. The linearized Langmuir Type I equation showed the highest correlation for the treated sample while the untreated sample was best modeled by the Langmuir Type II equation. The calculated maximum sorption capacity, $q_m$ and equilibrium constant $K_L$ varied among linear forms. This variation may have been the result of induced errors during linearization [24]. To further assess the goodness of fit, parameters obtained from linearization were used to generate theoretical equilibrium curves and subsequently compared to primary experimental data using the error functions presented in Table 4. The Relative Percent Error, RPE, Marquardt's Percent Standard Deviation, MPSD, and Hybrid Error Function, HYBRID verified the superiority of the Langmuir Type I equation in simulating the treated samples (Table 6). The MPSD and HYBRID functions revealed that the Langmuir Type III provided a better simulation of the untreated sample while the RPE function supported the Type II model. To explicate this variance, simulation of the data was performed using non-linear regression analysis, which is often considered a more robust method of optimization. This analysis was performed using the classical Langmuir non-linear equation. The results for the untreated and treated biosorbents are presented in Tables 7 and 8 respectively. A comparison of the goodness of fit using error values presented in Table 5 reveal that regression by the linear forms of the Langmuir equation are able to produce a slightly more precise simulation over that of non-linear regression.

**Table 1. Two-Parameter Isotherm Models**

| Isotherm | Non-linear equation | Linear expression | Equation number |
|---|---|---|---|
| Langmuir Type 1 | $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ | $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$ | (2) |
| Langmuir Type II (Lineweaver-Burk) | | $\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}$ | (3) |
| Langmuir Type III (Eadie-Hofstee) | | $q_e = q_m - \frac{q_e}{K_L C_e}$ | (4) |
| Langmuir Type IV (Scatchard) | | $\frac{q_e}{C_e} = K_L q_m - K_L q_e$ | (5) |
| Freundlich Equation | $q_e = K_F (C_e)^{\frac{1}{n_F}}$ | $log(q_e) = \log(K_F) + \frac{1}{n_F}\log(C_e)$ | (6) |

**Table 2. Three-Parameter Isotherm Models**

| Isotherm | Non-linear equation | Equation number |
|---|---|---|
| Redlich-Peterson | $q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{g_{RP}}}$ | (7) |
| Sips | $q_e = \frac{q_s (a_s C_e)^{n_s}}{1 + (a_s C_e)^{n_s}}$ | (8) |

**Table 3. Separation Factor**

| **$R_L$ Value** | **Nature of Process** |
|---|---|
| $R_L > 1$ | Unfavourable |
| $R_L = 1$ | Linear |
| $0 > R_L > 1$ | Favourable |
| $R_L = 0$ | Irreversible |

**Table 4. Error Functions**

| Error Functions | Expression | Equation number |
|---|---|---|
| Relative Percent Error (RPE) | $RPE\% = \frac{\sum\left[\left\|(q_e)_{predicted} - (q_e)_{experimental}\right\| / (q_e)_{experimental}\right]*100}{N}$<br>where $N$ is the number of experimental points | (11) |
| Marquardt's Percent Standard Deviation (MPSD) | $MPSD = 100\sqrt{\frac{1}{N-P}\sum_{i=1}^{N}\left[\frac{(q_{e_i})_{experimental} - (q_{e_i})_{predicted}}{(q_{e_i})_{experimental}}\right]^2}$<br>where $N$ is the number of experimental points and $P$ is the number of parameters in the regression model. | (12) |
| The Hybrid Error Function (HYBRID) | $HYBRID = \frac{100}{N-P}\sum_{i=1}^{N}\left[\frac{\left((q_{e_i})_{experimental} - (q_{e_i})_{predicted}\right)^2}{(q_{e_i})_{experimental}}\right]$<br>where $N$ is the number of experimental points and $P$ is the number of parameters in the regression model. | (13) |

**Table 5. Langmuir isotherm parameters obtained by linear regression for *Fomes fasciatus* uptake of Cu (II) ions**

| Biosorbent | Isotherm Model | $q_m$ | $K_L$ | $r^2$ |
|---|---|---|---|---|
| Untreated *Fomes fasciatus* | Langmuir Type I | 0.0260 | 0.0777 | 0.9965 |
| | Langmuir Type II | 0.0276 | 0.0652 | 0.9964 |
| | Langmuir Type III | 0.0270 | 0.0687 | 0.9695 |
| | Langmuir Type IV | 0.0152 | 0.0660 | 0.9695 |
| | | | | |
| Treated *Fomes fasciatus* | Langmuir Type I | 0.0317 | 0.1871 | 0.9991 |
| | Langmuir Type II | 0.0295 | 0.2536 | 0.9746 |
| | Langmuir Type III | 0.0306 | 0.2267 | 0.9244 |
| | Langmuir Type IV | 0.0287 | 0.2090 | 0.9244 |

The Freundlich isotherm is a special case for sorption unto heterogeneous surfaces. The equation therefore describes reversible adsorption and is not restricted to the formation of a monolayer [18]. The applicability of the classical empirical Freundlich equation to simulate *Fomes fasciatus* uptake of Cu (II) ions was assessed first by linear regression using equation (6). The Freundlich constant, $K_F$ is related to sorption affinity [13] and $n_F$ characterizes the heterogeneity of the system. The parameters for both untreated and treated *Fomes fasciatus* were obtained by linear plots of $log\ (q_e)$ vs. $log\ (C_e)$. The coefficients of determination, for both untreated and treated biosorbents were 0.9286 and 0.9325 respectively. This reveals that the biosorption process closer conforms to the Langmuir assumption. Further, this implies that the coverage of Cu (II) ions onto the biosorbent exhibits the characteristics of monolayer surface formation.

The precision of the two-parameter Langmuir models to the primary equilibrium data is sufficient to permit mechanistic inferences. The Langmuir isotherm is based on the assumption that points of valency exist on the surface of the sorbent and that each of these sites is capable of adsorbing one molecule. Consequently, the adsorbed layer will be one molecule thick [19]. Furthermore, it assumes that all the sorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the sorption of molecules at an adjacent site. Primary equilibrium data obtained at constant temperature for the biosorption of Cu (II) by untreated and treated *Fomes fasciatus* are represented in Figure 1. The plots depict a similar trend exhibited by both untreated and treated biosorbents. Visually, it is observed that the treated *Fomes fasciatus* possess a greater affinity for the Cu (II) ions over that of the untreated *Fomes fasciatus*. The shape of both equilibrium curves shows the trend of levelling out at higher concentrations. This indicates, according to Langmuir's assumption, the completion of a monolayer in the concentration range.

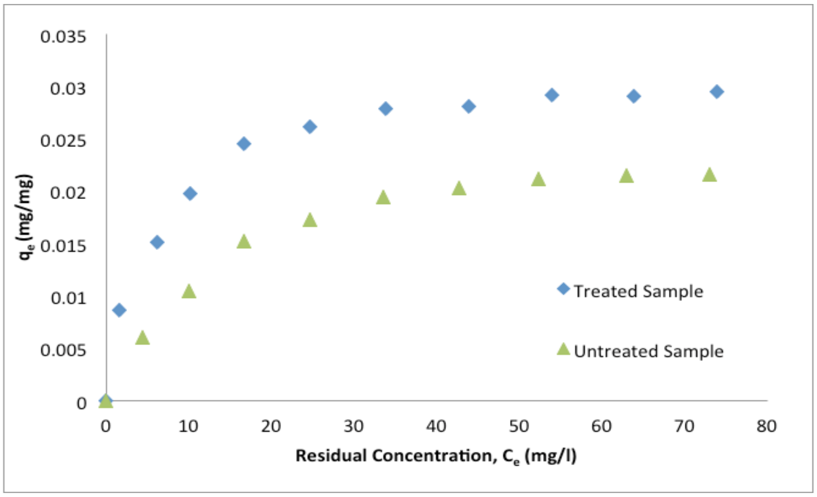

**Fig. 1 Primary equilibrium curve depicting the sorption of Cu (II) onto untreated and treated *Fomes fasciatus***

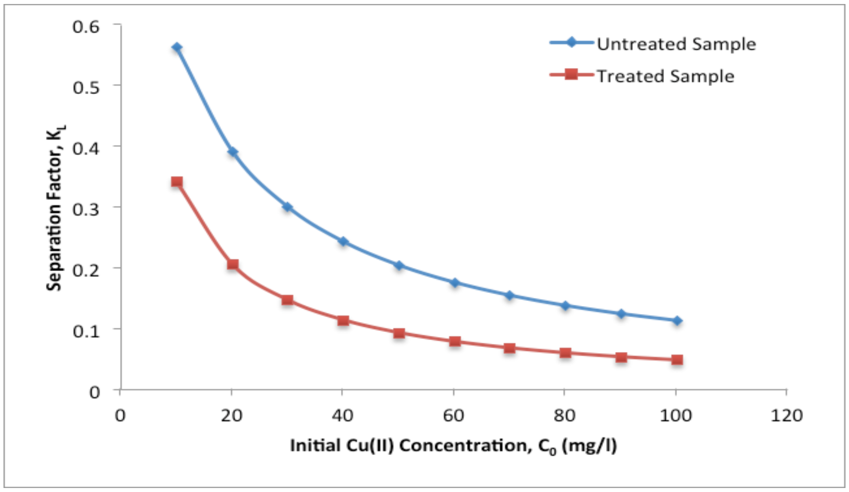

**Fig. 2 Curve showing variation in separation factor for untreated and treated *Fomes fasciatus***

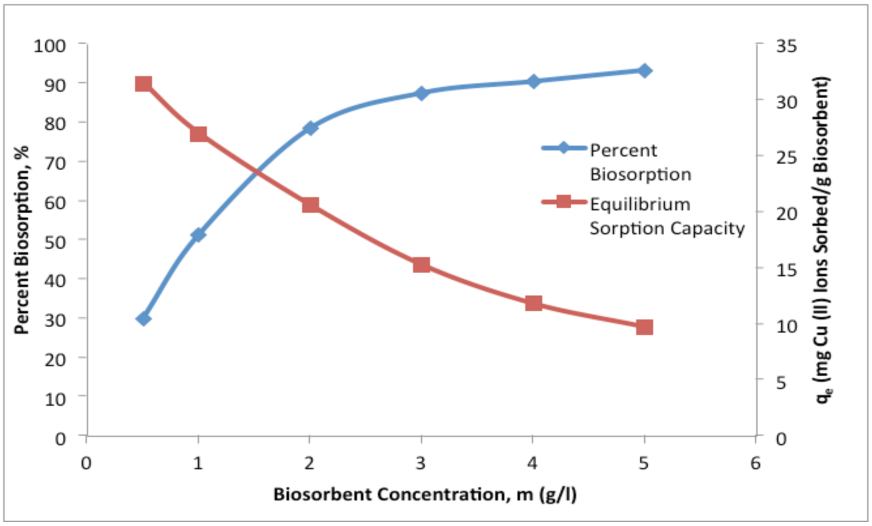

**Fig. 3 Curve showing effect of biosorbent dose on the uptake of Cu (II) ions by treated *Fomes fasciatus***

**Table 6. Comparison of non-linear experimental curve to theoretically generated non-linear Langmuir curve**

| Biosorbent | Model | RPE | MPSD | HYBRID |
|---|---|---|---|---|
| Untreated *Fomes fasciatus* | Langmuir Type I | 3.5093 | 4.9721 | 0.0027 |
| | Langmuir Type II | 2.6804 | 3.8570 | 0.0026 |
| | Langmuir Type III | 2.8731 | 3.7622 | 0.0023 |
| | Langmuir Type IV | 44.731 | 50.764 | 0.4388 |
| | | | | |
| Treated *Fomes fasciatus* | Langmuir Type I | 4.0684 | 7.4883 | 0.0067 |
| | Langmuir Type II | 5.8671 | 8.3001 | 0.0130 |
| | Langmuir Type III | 4.6081 | 7.4950 | 0.0090 |
| | Langmuir Type IV | 8.7660 | 10.6670 | 0.0235 |

**Table 7. Comparison of isotherm models using non-linear regression to simulate untreated *Fomes fasciatus* uptake of Cu (II) ions**

| Isotherm | Constants | | RPE | MPSD | HYBRID |
|---|---|---|---|---|---|
| Redlich-Peterson | $a_{RP}$ | 0.0249 | 1.8203 | 2.9030 | 0.0008 |
| | $K_{RP}$ | 0.0015 | | | |
| | $g_{RP}$ | 1.1917 | | | |
| Sips | $a_S$ | 0.0891 | 2.4852 | 3.8511 | 0.0014 |
| | $q_S$ | 0.0241 | | | |
| | $n_S$ | 1.2426 | | | |
| Langmuir | $q_m$ | 0.0264 | 3.2865 | 4.5667 | 0.0024 |
| | $K_L$ | 0.0750 | | | |
| Freundlich | $K_F$ | 0.0051 | 10.6371 | 17.3401 | 0.0251 |
| | $n_F$ | 2.8047 | | | |

**Table 8. Comparison of isotherm models using non-linear regression to simulate treated *Fomes fasciatus* uptake of Cu (II) ions**

| Isotherms | Constants | | RPE | MPSD | HYBRID |
|---|---|---|---|---|---|
| Redlich-Peterson | $a_{RP}$ | 0.1952 | 4.1792 | 7.5371 | 0.0064 |
| | $K_{RP}$ | 0.0059 | | | |
| | $g_{RP}$ | 0.9846 | | | |
| Sips | $a_S$ | 0.1603 | 3.5906 | 5.5922 | 0.0043 |
| | $q_S$ | 0.0335 | | | |
| | $n_S$ | 0.8756 | | | |
| Langmuir | $q_m$ | 0.0320 | 4.2097 | 8.0833 | 0.0069 |
| | $K_L$ | 0.1736 | | | |
| Freundlich | $K_F$ | 0.0105 | 9.2022 | 14.9429 | 0.0283 |
| | $n_F$ | 3.8981 | | | |

The Langmuir constant $K_L$ is related to the binding energy or sorption energy coefficient, where a high value of $K_L$ indicates a high affinity [10]. From Table 5 it is observed that Cu (II) ions exhibit a significantly stronger affinity for the treated biosorbent over that of the untreated. Using the Langmuir's constant $K_L$ and equation (9), the shape of the isotherm was further evaluated by the dimensionless constant separation factor ($R_L$). A plot of $R_L$ verses initial Cu (II) concentration for both treated and untreated samples are presented in Figure 2. Within the range of initial concentration investigated, the value of $R_L$ for both the treated and untreated biosorbent lies below 1, which according to Table 3, implies that both biosorbents produces a favourable isotherm. The values of $R_L$ continue to decrease as initial concentration is increased, indicating an increase in the feasibility of the reaction. For any given initial concentration within the range of the experiments, the treated biosorbent produces a lower separation factor implying a relative decrease potential to leaching.

## Equilibrium Analysis using Three-Parameter Models

Using non-linear regression, equilibrium data simulation was also carried out using both the Redlich-Peterson and the Sips three-parameter models (Table 2). The results for untreated and treated specimens are also presented in Tables 7 and 8 respectively. The empirically based Redlich–Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich isotherms [5]. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator enabling its application over a wide concentration range. The model produces the constants $K_{RP}$, $a_{RP}$ and the exponent $g_{RP}$. This equation reduces to a linear isotherm at low surface coverage, to the Freundlich isotherm at high sorbate concentration and to the Langmuir isotherm when $g_{RP}$=1 [1].

Among the models tested, the Redlich–Peterson model produced the greatest correlation to the untreated biosorbent data. The exponent, which usually varies between 0 and 1, was found to be 1.19, indicating a deviation from the norm. Interpretation was therefore restricted to the mathematical representation of the data and no mechanistic inference was drawn.

The Sips model is another combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the rising adsorbate concentration associated with the Freundlich isotherm model [5]. The equation produces the constants $q_S$ which is the equilibrium sorption capacity, $a_S$ is the affinity constant for adsorption and $n_S$ is the index of heterogeneity. When $n_S = 1$, the Sips equation reduces to the Langmuir equation and implies a homogeneous sorption process. From Tables 7 and 8, it is observed that this equation produced the highest correlation to the treated biosorbent. The exponent was found to be 0.87 indicating the equation is approaching the Langmuir model and implies a homogeneous process. Error analysis further reveals that the tested three-parameter models produce a marginally better simulation due to the introduction of the exponent. Though very little mechanistic inferences can be drawn, the precision of the simulation is well suited for the development of predictive model.

## Effect of Hot-Alkali Pre-treatment

The pre-treatment of the biosorbent by alkaline solution at an elevated temperature dissolve proteins, hydrolyse lipids and deacetylate chitin to chitosan [14]. Analysis of equilibrium data using the Langmuir model revealed that the deacetylation of *Fomes fasciatus* resulted in an increase in equilibrium sorption capacity, $q_m$ with an accompanied increase in binding energy $K_L$. Further, using equation (10), this monolayer surface coverage by Cu (II) ions was used to calculate the specific surface area. The calculation revealed a 17.5 per cent increase in available binding sites after treatment. The specific surface area of untreated samples was found to be 4.06 $m^2/g$, while the treated sample was 4.77 $m^2/g$. The cell wall matrix of forest macro-fungus has been previously reported to be responsible for the uptake of Cu (II) ions [14]. Thus the increase in the metal uptake and specific surface area after deacetylation may be attributed to the unmasking of cellular groups, which were not previously participating in the sorption process. The accompanying increase in binding energy may therefore imply a shift in the mechanism or mechanisms of biosorption.

## Effect of Mass of Biosorbent

The effect of varying biosorbent dose was investigated at a constant initial Cu (II) concentration of 50 mg/l. Figure 3 shows the effect of sorbent dose as a function of both the percentage sorbed at equilibrium and the amount sorbed per unit weight of biosorbent. The figure reveals an increase in removal from 30 per cent to 88 per cent as sorbent dose was increased from 0.5 g/l to 3.0 g/l. This increase in sorbed ions is attributed to the increase in specific surface area. Beyond a sorbent dose of 3.0 g/l there was only a marginal increase observed. This behaviour is due to the binding of almost all ions to the sorbent and the establishment of equilibrium between the ions bound to the sorbent and those remaining in solution [17]. Figure 3 also reveals that as biosorbent dose increases, the amount of Cu (II) ions sorbed per gram of biosorbent decreases. In spite of the significant increase in biosorbent dose and thus, specific surface area, 100 per cent removal is not achieved. This further implies that concentration gradient is a dominant driving forces for biosorption unto *Fomes fasciatus*. Thus, during batch treatment, greater process efficiency and economy can be accomplished by using multiple small batches rather than a single large batch [17].

## CONCLUSION

The effect of hot-alkali treatment on the biosorptive performance of *Fomes fasciatus* was assessed through batch equilibrium studies. Analysis of equilibrium data was performed using two and three parameter isotherm models. Deacetylation of *Fomes fasciatus* through hot-alkali treatment was successful in increasing the affinity of the biosorbent for Cu (II) ions. Alkali treatment resulted in a 17.5 per cent increase in equilibrium sorption capacity and an accompanied increase in biosorbent specific surface area from 4.06 $m^2/g$ to 4.77 $m^2/g$. For a particle geometric mean size of 0.5 mm, the highest process efficiency was realized using a biosorbent dose of 3 g/l.

The three-parameter models produced the highest correlation to the experimental data. The Redlich-Peterson model produced the highest correlation to the untreated sample, while the Sips model conform best to the treated sample. Among the two-parameter models tested both treated and untreated samples followed the Langmuir assumption of monolayer sorption with homogeneous surface characteristics. Further, the treated sample was well represented by the Type I linearized Langmuir model while the Type III best represented the untreated sample. The precision of the model was sufficient to enable mechanistic suppositions.

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