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Comparism of Biosorption of Copper ions by immobilised *Bacillus circulans* and *Saccharomyces Cerevisiae* from Wastewater

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Received: February 14, 2025, Accepted: April 28, 2025

Abstract: Copper poses a great risk to living organisms in the environment, calling for an alternative environmentally friendly and cost-effective technique such as microbial sorption (biosorption) for its remediation from aqueous solution. The potential of lyophilised immobilised *Bacillus circulans* and *Saccharomyces Cerevisiae* to serve as biosorbents for biosorption of copper ions from aqueous solution in a batch process system were investigated. The biosorbents developed were characterised using Scanning electron microscope and Fourier transform infrared spectroscopy. The effects of environmental parameters on biosorption of copper ions onto immobilised biosorbents of *Bacillus circulans* and *Saccharomyces Cerevisiae* in a batch process system were also compared and investigated. The optimum parametric values such as pH, contact time, biosorbent dosage and initial concentration for: Copper ions *onto Bacillus circulans* were measured as 4 , 60 min, 1.0 g and 80 mg/l, respectively; Copper ions onto *Saccharomyces Cerevisiae* were recorded as 3 , 80 min, 0.4 g and 100 mg/l, respectively. The biosorption mechanism shows better fitness of Freundlich isotherm model and the kinetics follows Pseudo second order for both immobilised Bacillus circulans and *Saccharomycesc cerevisiae* for copper ions contacting. The results show that immobilised *Bacillus circulans* and Saccharomyces Cerevisiae are highly efficient in the removal of copper ions from aqueous solution. The biosorption capacity and percentage removal for copper ions onto *Bacillus circulans* gives better optimum performance to *Saccharomyces cerevisiae* contacting.

Keywords: Biosorption, *Saccharomyces cerevisiae, Bacillus* circulans, Environmental parameters optimisation,

Introduction

Biosorption generally known as Bioremediation involves the use of living organisms (biological systems) which include both plant and animals to detoxify and remove or reduce the environmental pollutants from air, soil and water (Guo, *et al.*, 2010; Gargouri *et al.*, 2011; Adams *et. al*., 2015; Oyetibo *et al.*, 2017, Luka *et al.*, 2021; Luka *et al.*, 2024). Living and dead metabolically inactive microorganism or their derivatives can remove metal ions from a polluted environment (Abbas *et al.*, 2014; Farhan and Khadom, 2015; Luka *et al.*, 2022; Luka *et al.*, 2024). To be precise, Biosorption is a passive, rapid, reversible and independent metabolic energy process carried out by active or inactive microorganisms (Vendruscolo *et al.*, 2017; Luka *et al.*, 2024).

The constant wide spread of heavy metals (copper ions) into the aquatic environment can be attributed to anthropogenic activities and is one of the major problems of the ecosystems today ((Fu and Wang, 2011; Macek and Mackova, 2011; Wu *et al.*, 2012; Wang, *et al.*, 2014; Jones *et al.*, 2016; Ogunsile and Bamgboye, 2017; Luka *et al.*, 2024). Treatment of water before use is the only solution to related water-borne diseases easily identified with contaminated or polluted water (Jones *et al.*, 2016). For instance, Copper ions can cause diarrhea, dizziness and neurotoxicity (Abbas *et al.*, 2014).

Various techniques have been implemented for removal of heavy metals such as ion exchange, chemical precipitation, membrane filtration and reverse osmosis. These methods have high cost for energy and maintenance and the generation of toxic byproducts; and they are not environmentally friendly compared to biosorption (Colak *et al.*, 2011; Luka *et al.*, 2024). The use of freely suspended microbial biomass has its negative effects which includes small particle size, low mechanical strength and problems associated with separation of biomass from the effluent (White *et al.*, 1995). Due to these reasons, immobilised *Bacillus Circulans and Saccharomyces Cerevisiae* were used as biosorbents for the biosorption in a Batch System.

The aim of this study is to compare the potential of immobilised *Bacillus circulans* and *Saccharomyces Cerevisiae* to remove copper ions from wastewater in a Batch System as well as investigating the environmental parameters affecting the biosorption.

Materials and Methods

Preparation of Stock Solution and Serial Dilution

A stock solution ($100\ mg/l$) of copper ions was prepared from copper nitrate trihydrate $(Cu(NO_3)_2.3H_2O)$. To determine the potential of immobilised *Bacillus circulans* and *Saccharomyces Cerevisiae* to remove copper ions from wastewater and for optimisation of some selected environmental factors in a batch process system. Synthetic wastewater was prepared by serial dilution of the stock solution of Copper ions solution each into distilled water with the desired metal ions solution ranged between $20 - 100\ mg/l$ and Nitrate salt was used as the counter ions for metal ions because of its low tendency to form complexes (Amirnia, 2015; Luka *et al.*, 2021; Luka *et al.*, 2023).

Immobilisation of Biosorbent

Entrapment method that involved drop wise addition of biomass suspended in polymer matrix as adapted by Kumar *et al.*, (2011); Ilamathi *et al.*, (2014); Luka *et al.*, (2021) and Luka *et al.*, (2023) was used. The beads were produced when the alginate biomass slurry was introduced drop wise into $250\ ml$ of dissolve dehydrate $0.1\ M\ CaCl_2$ using $20\ ml$ syringe for polymerisation. The resultant beads after production were kept using Haier Thermocool Refrigerator HRD – 231SX at 4 ℃ (freezer) in $CaCl_2$ solution for $12 - 14\ h$ for hardening as depicted in Plate 1. It was then washed with $500\ ml$ distilled water twice. The drained beads were spread on a dryer tray using GENLAB ENGLAND – N535 oven and kept at $80 - 100$ ℃ for an hour and later adjusted to 40 ℃ till the whole beads were dried for avoidance of burning sensation to the bead produced as shown in Plate 2. After drying, each strain of immobilised biomass bead was kept inside tight bottle for future use as biosorbent.

Plate 1: Fresh and Life Immobilised Biosorbent before Heat Killing

Plate 2: Washed and Drained Beads Spread on a Dryer Tray ready for Drying in an Oven

Characterisation of Immobilised Bacillus circulans

The characterisation was done before and after biosorption of copper ions, respectively. PHENOM Prox Netherland Scanning electron microscope (SEM) gives information on surface morphology of each biosorbent of immobilised *Bacillus circulans* and *Saccharomyces Cerevisiae*, respectively; while AGILENT TECHNOLOGIST USA – Cary 630 Fourier transformed infrared spectroscopy (FTIR) gives information on functional groups presence and chemical composition of each biosorbent of immobilised *Bacillus circulans* and *Saccharomyces Cerevisiae,* respectively (Luka *et al.*, 2021; Luka et al., 2023).

Batch Process System

Batch process system that was used in this study are Erlenmeyer conical flasks of $100\ ml$. Five flasks for each metal ions were incubated in a rotary shaker type at $150\ (rpm)$ and room temperature (32 ℃) for $100\ min$ to obtain equilibrium for each biosorbate and biosorbent used to monitor a particular parameter under investigation. The mixtures were decanted and the residual concentration of each Copper ions solution after biosorption were determined using VGP210 - AAS, respectively. The uptake value at equilibrium was calculated using equation (1) (Colak *et al.*, 2013; Dobaradaran *et al.*, 2016; Ahmad *et al.*, 2018; Luka *et al.*, 2021):

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

Where, q_e is the uptake of metal (mg/g), C_i and C_e are the initial and equilibrium metal concentrations in the water (mg/l) respectively; V is the volume of solution (l) and m is the mass of adsorbent (g). The removal percentage (R) of the metal ion by the biosorbent was achieved using equation (2) (Galedar and Younesi, 2013; Ahmad et al., 2018):

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100$$
(2)

2.5 Optimisation of environmental Parameters

Optimum values of pH, biosorbent doses, contact time and initial metal concentration (Luka *et al.*, 2024) were determined for copper ions biosorption in batch mode. The optimum value of pH for each metal ions at an initial concentration of $100\ mg/l$ and $1.0\ g$ biosorbent in $50\ ml$ of metal solution at room temperature (32 ℃) for $100\ min$ at pH varying from $3.0 - 7.0$ using HANNA INSTRUMENTS - $pHep^{(R)}$ pH meter were obtained by adding $0.1\ M\ NaOH$ or HCl. The effect of contact time was investigated at room temperature, each metal ion initial concentration of $100\ mg/l$ and $1.0g$ biosorbent in $50\ ml$ of metal solution at 32 ℃ for $100\ min$ and an optimised pH. The effect of contact time was studied by varying at $20, 40, 60, 80$ and $100\ min$, room temperature, initial concentration of $100\ mg/l$ and $1.0g$ biosorbent in $50\ ml$ of metal solution. Furthermore, effect of biosorbent dosage were optimised by using biosorbents amounts of $0.2, 0.4, 0.6, 0.8\ and\ 0.1\ g$ in $50\ ml$ of an initial metal ions concentration of $100\ mg/l$ each, at room temperature and at optimised pH as well as contact time. For optimisation of initial metal concentration, biosorption investigation at optimised parametric values were achieved with initial metal ions concentrations each of value $20, 40, 60, 80\ and\ 100\ mg/l$ respectively (Samuel et al., 2013). In batch system, the mixture of biosorbent and wastewater were decanted and the clear supernatant from aqueous sample were analyzed using VGP210 - Atomic absorption spectroscopy for copper ions concentration. The final concentration of each metal ions was measured using Standard method for examination of water and wastewater as adapted by Luka *et al.*, (2021).

Results and Discussion

Characterisation of Immobilised *Bacillus circulans* and *Saccharomyces cerevisiae*

SEM analysis of immobilised Bacillus circulans

The SEM images results for biosorbents before and after biosorption of two different biosorbates are presented in Plates 3 - 6. Plates 3 - 4 show the change in morphology displayed by *Bacillus circulans* before and after biosorption with copper ions, respectively.

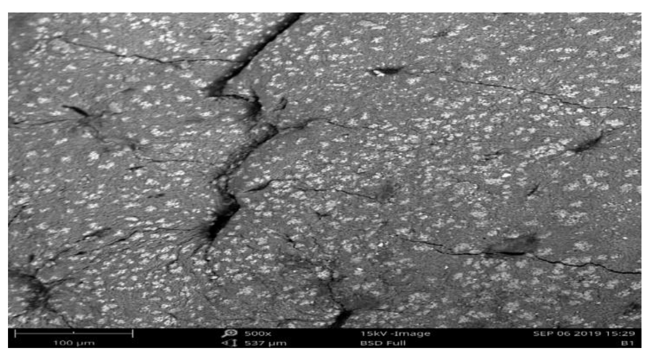

Plate 3: SEM Image of Immobilised *Bacillus Circulans* before Biosorption at 500x magnification

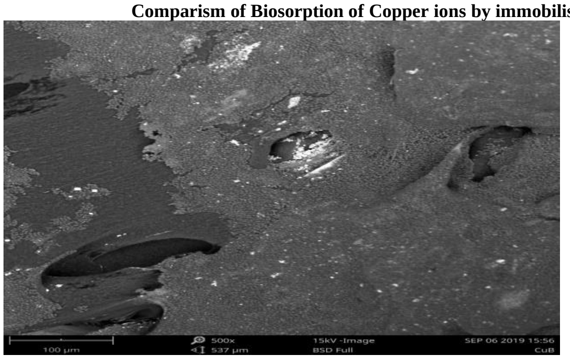

Plate 4: SEM Image of Immobilised *Bacillus Circulans* for Copper ions after biosorption at 500x magnification

The results shown by SEM images of immobilised *Bacillus circulans biosorbent* for copper ions for each analysis clearly show a change in the surface morphology of the biosorbents after exposure to biosorbates. The surface of biosorbents were observed to be made up of heterogeneous structure and micropores which were known for more biosorption and internally bioaccumulation of biosorbates. The results of this studies show similarity to that of Ririhena *et al*., (2018) and Luka *et al.,* (2021) who reported that SEM of *Saccharomyces cerevisiae* after biosorption show changes and have more holes than before biosorption which look more hydrated and plumper. This morphological change occurs due to copper ions biosorption at the cell wall.

3.1.2 SEM analysis of immobilised *Saccharomyces Cerevisiae*

Plates 5 - 6 display the images of immobilised *Saccharomyces cerevisiae biosorbent*. Showing the change in morphology before and after biosorption with copper ions, respectively.

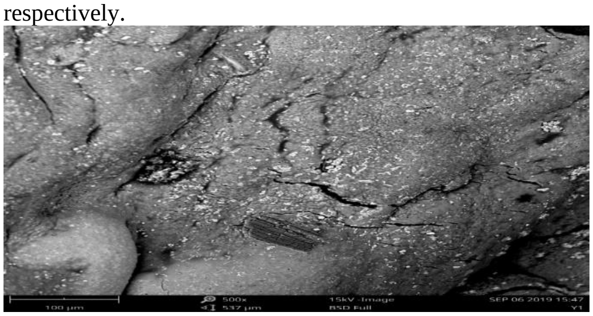

Plate 5: SEM Image of Immobilised *Saccharomyces Cerevisiae* before Biosorption at 500x magnification

Plate 6: SEM Image of Immobilised *Saccharomyces Cerevisiae* for Copper ions after biosorption at 500x magnification

The surface of Saccharomyces *cerevisiae* before biosorption (Plate 5) contains many traps but shorter than that of *Bacillus circulans* (Plate 3). The micrograph of *Bacillus circulans* before biosorption has tinier micropores on the surface to that of *Saccharomyces cerevisiae.* After biosorption of copper ions onto *Bacillus circulans* and onto Saccharomyces *cerevisiae*, the surface structure of both biosorbents were transformed significantly as shown in Plates 4 and 6 for *Bacillus circulans* and *Saccharomyces cerevisiae* biosorbents, respectively. Concerning copper (Plates 4 and 6), the micropores structure become smoother after biosorption compared to before biosorption of the biosorbate onto the biosorbents (Abdul Raffar *et al.*, 2015; Nadeem *et al.*, 2016).

FTIR analysis of immobilised Bacillus circulans

The results of the FTIR Spectra for biosorbents before and after biosorption with biosorbate are presented in Figures 1 - 4.

Figures 1 – 2 show the trend obtained for *Bacillus circulans*

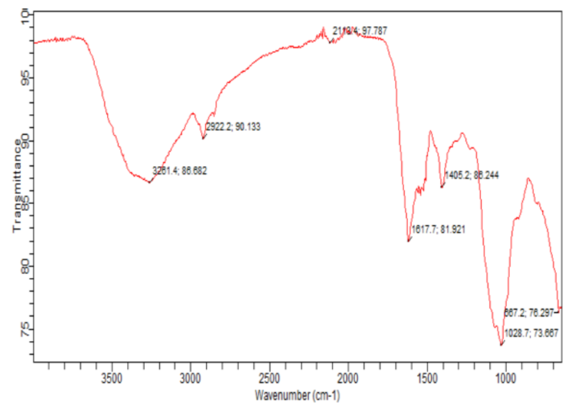

Figure 1: FTIR Spectra of Immobilised *Bacillus Circulans* before Biosorption

The FTIR spectra for *Bacillus circulans* (Figure 1) showed the functional groups that are present in the biosorbent before biosorption. The major peaks were noted at $3261.4, 2922.2, 2110.4, 1617.7, 1405.2, 1028.7$ and $667.2\ cm^{-1}$; this implies the assigned functional group are $-OH$ stretch for carboxylic acid, $C-H$ stretch for aldehyde, $C \equiv C$ stretch for alkyne, $N-H$ bend for amine, $-OH$ bend for phenol/ tertiary alcohol, $C-N$ stretch for primary amine and $-OH$ for alcohol out of phase bend, respectively (Hossian, 2013; Kariuki *et al*., 2017).

Figures 3 – 4 give the outcome of using *Saccharomyces cerevisiae as* biosorbent.

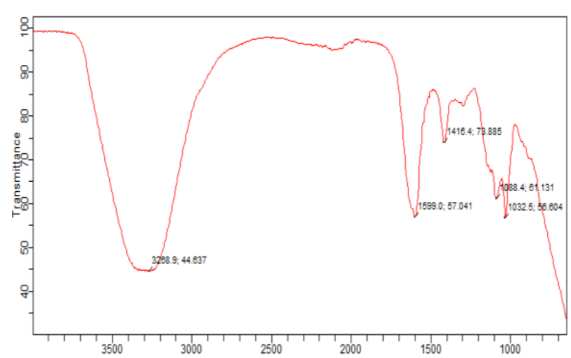

Figure 2: FTIR Spectra of Immobilised *Bacillus Circulans* for Copper ions after biosorption

The peaks shifting assigned to copper ions after biosorption were $3268.9, 1599.0, 1416.4, 1088.4, 1032.5\ cm^{-1}$. This verifies the interaction between hydroxyl, carboxyl, amine, phenol and alcohol functional groups with Cu^{2+}.

FTIR analysis of immobilised Saccharomyces Cerevisiae

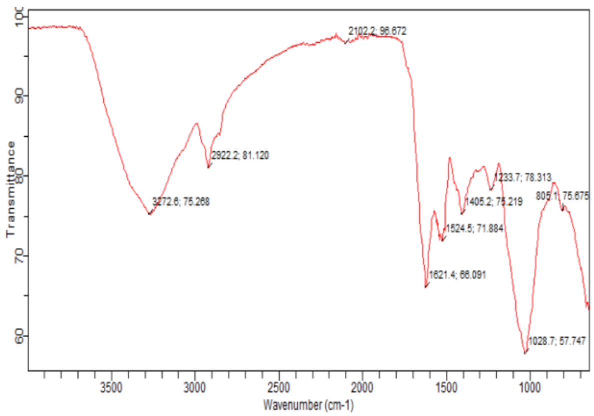

Figure 3: FTIR Spectra of Immobilised *Saccharomyces Cerevisiae* before Biosorption

The FTIR spectra of *Saccharomyces cerevisiae* biosorbent before biosorption (Figure 3) were recorded at $3272.6, 2922.2, 2102.2, 1621.4, 1405.2, 1233.7, 1028.7$ and $805.1\ cm^{-1}$; the corresponding functional groups are $-OH$ stretch for carboxylic acid, $C-H$ stretch for aldehyde, $C \equiv C$ stretch for alkyne, $N-H$ bend for amine, $-OH$ bend for phenol/ tertiary alcohol, $C-O$ stretch for alcohol/carboxylic acids/esters/ethers, $C-N$ stretch for primary amine and $C-H$ for aromatic out of plane bend, respectively.

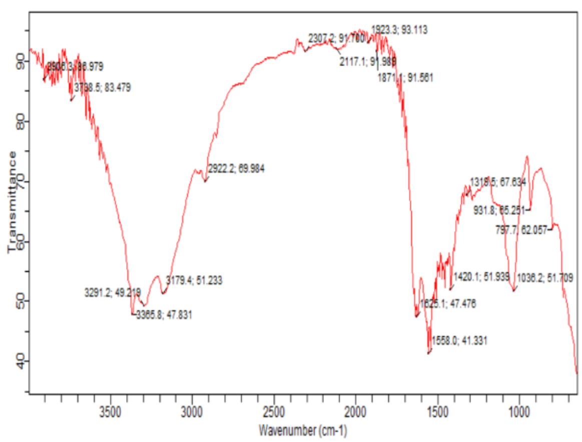

Figure 4: FTIR Spectra of Immobilised *Saccharomyces Cerevisiae* for Copper ions after biosorption

A new FTIR peaks (Figure 4) were found at 3906.3, 3738.5, 3291.2, 3365.8, 3179.2, 2922.2, 2307.2, 2117.1, 1923.3, 1871.1, 1625.1, 1558.0, 1420.1, 1318.5, 1036.2, 931.8 and 797.7 cm^{-1} after biosorption of copper ions which differ from that of *Saccharomyces cerevisiae* biosorbents before biosorption (Hasan *et al.*, 2016; Nadeem *et al.*, 2016; Benjreid *et al.*, 2018).

Optimisation of environmental Parameters

The results for optimisation of environmental parameters affecting biosorption of copper ions onto immobilised *bacillus circulans* and *saccharomyces cerevisiae* which include pH of biosorbate, contact time, biosorbent dosage and initial concentration of biosorbate are presented in Figures 5 - 12, respectively. Figures 5 - 6, present optimum values of pH of biosorbate.

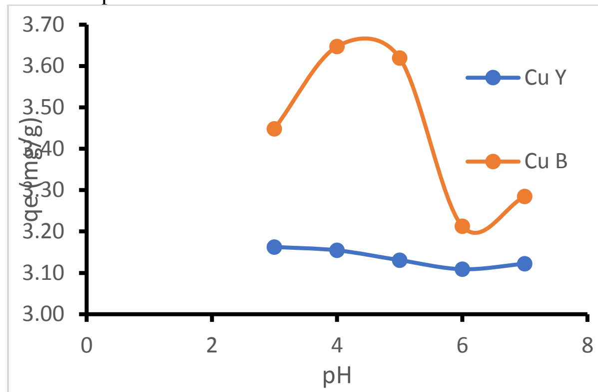

Figure 5: Effect of pH on Biosorption Capacity of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

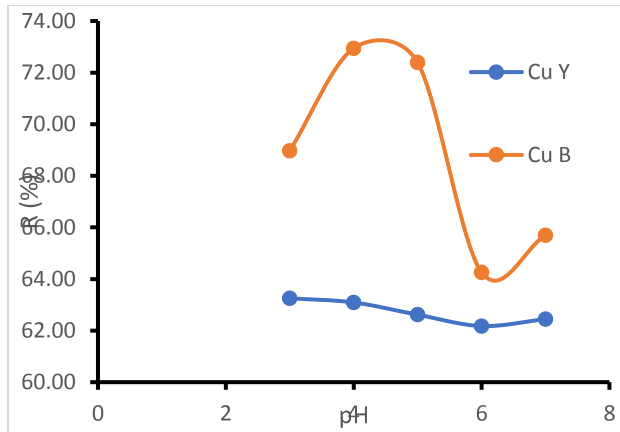

Figure 6: Effect of pH on Removal Percentage of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Regarding copper ions onto *Saccharomyces Cerevisiae* $(Cu\ Y)$ as biosorbent, maximum biosorption capacity (Figure 5) and percentage removal (Figure 6) were obtained at pH of 3 with values of 3.16 mg/g and 63.25 %, respectively. Whereas copper ions onto *Bacillus circulans* $(Cu\ B)$ as biosorbent measured maximum biosorption capacity (Figure 5) and percentage removal (Figure 6) at pH of 4 with values of 3.65 mg/g and 72.92 %, respectively. The results obtained are in line with Jones *et al.* (2016) which shows fluctuations in biosorption efficiency with a constant increase in pH of the biosorbates of Cd^{2+}, Fe^{2+}, Ni^{2+} and Zn^{2+} using Mucilage from *Dicerocaryum Eriocarpum* Plant as biosorbent.

The batch investigation on effect of contact time is presented in Figures 7 – 8 for copper and ions, chronologically.

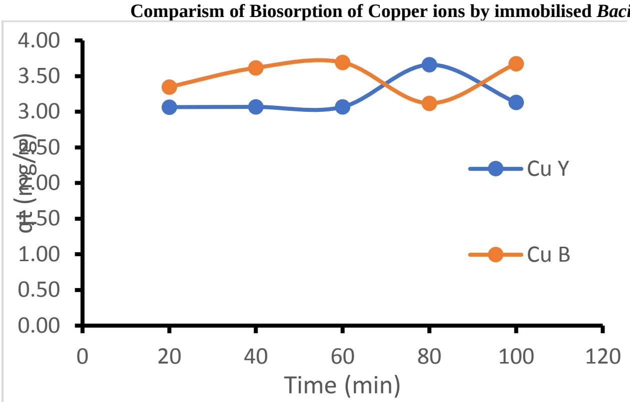

Figure 7: Effect of Contact Time on Biosorption Capacity of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

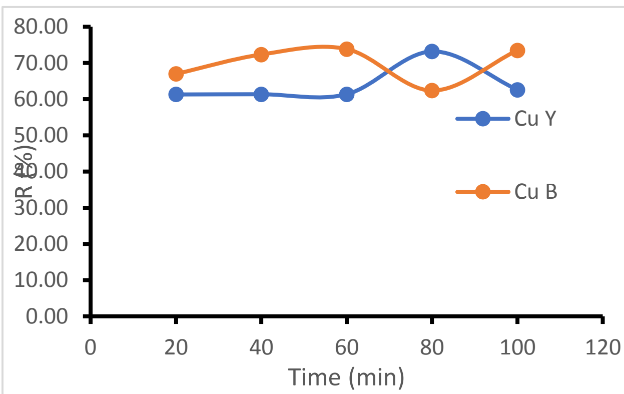

Figure 8: Effect of Contact Time on Removal Percentage of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Considering, copper ions, optimum biosorption capacity (Figure 7) and percentage removal (Figure 8) for *Saccharomyces cerevisiae* were observed at contact time of $80\ min$ with values of $3.66\ mg/g$ and $73.18\ \%$, respectively. Decrease was recorded for *Saccharomyces cerevisiae* at $100\ min$. Whereas biosorption capacity (Figures 7) and percentage removal (Figure 8) for copper ions onto *Bacillus circulans* increases from $20\ min$ to $60\ min$ and a decrease at $80\ min$. Therefore, maximum biosorption capacity and percentage removal were recorded at contact time of $60\ min$ with values $3.69\ mg/g$ and $73.85\ \%$, respectively. The decrease in biosorption capacity of copper ions (Figure 7) and percentage removal of copper ions (Figure 8) after optimum values were observed might be due to gradual exhaustion of the number of vacant site available. The results of this research show similarity to those of Colak *et al.* (2011), where Biosorption of lead from aqueous solutions by *Bacillus strains* possessing heavy-metal resistance as biosorbent show that larger number of vacant surface sites are available for biosorption in the initial stage and virtually remain constant with increase in contact time.

From contact time optimisation, the following can be drawn: the optimum values for copper ions were obtained at $100\ min$ and $60\ min$ using *Bacillus circulans* as biosorbent with optimum percentage removal values recorded as $73.85\ \%$. In addition, copper ions optimum percentage removal was found at $60\ min$. This is in agreements with the explanation given by Jones et al. (2016) for $Cd^{2+}, Fe^{2+}, Ni^{2+}$ and Zn^{2+} ions using Mucilage from *Dicerocaryum Eriocarpum* Plant as biosorbent, where biosorption increased rapidly at the beginning and became very slow or steady with time.

The results for optimum biosorbent dosage are shown in Figures 9 - 10.

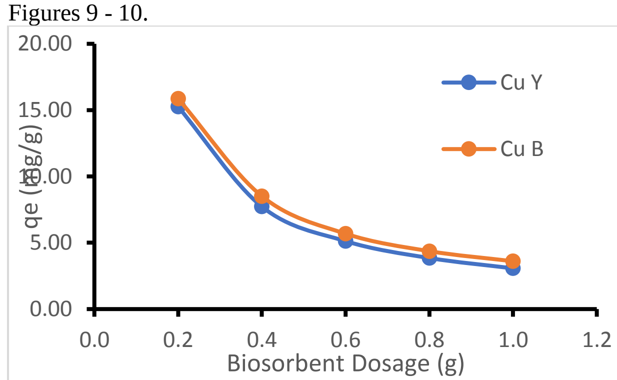

Figure 9: Effect of Biosorbent Dosage on Biosorption Capacity of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

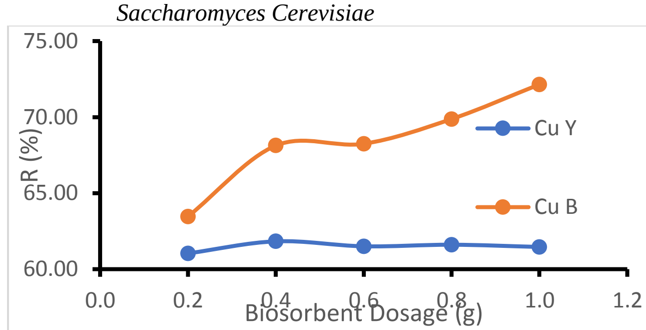

Figure 10: Effect of Biosorbent Dosage on Removal Percentage of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Secondly, copper ions as recorded a decrease in the values of biosorbent capacity with increase in the values of biosorbent dosage from $0.2\ g$ to $1.0\ g$. The maximum biosorption capacity of copper ions onto *Bacillus circulans* (Cu B) and copper ions onto *Saccharomyces cerevisiae (Cu Y)* were observed at $0.2\ g$ as depicted in Figure 9 with value $15.87\ mg/g$ and $15.26\ mg/g$, respectively. The highest percentage removal for copper ions onto *Bacillus circulans* (Cu B) and copper ions onto *Saccharomyces cerevisiae (Cu Y)* were measured at $1.0\ g$ with value of $72.15\ \%$ and at $0.4\ g$ with value of $61.83\ \%$ as displayed in Figure 10, respectively.

Based on the results recorded on optimisation of biosorbent dosage the following can be established: The values of biosorption capacity decreases for copper ions using either immobilised *Bacillus circulans* or *Saccharomyces cerevisiae* as biosorbent with increases in biosorbent dosage. The maximum percentage removal using *Saccharomyces cerevisiae* biosorbent was recorded as $61.83\ \%$ at $0.4\ g$ for copper ions; while, maximum percentage removal using *Bacillus circulans* biosorbent was measured as $72.15\ \%$ at $1.0\ g$ also, for copper ions.

The illustration for effect of initial concentration of biosorbate on biosorption capacity and percentage removal are presented in Figures 11 – 12.

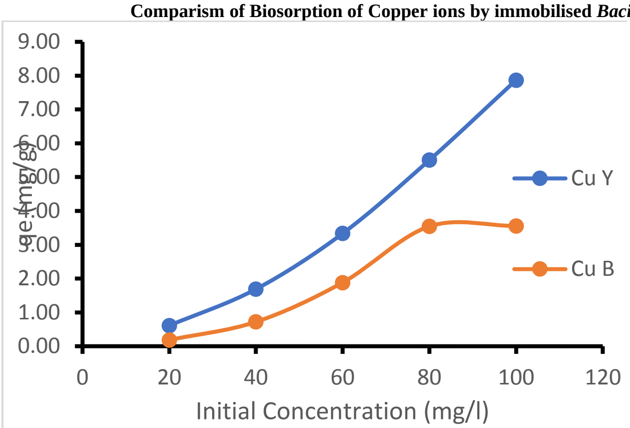

Figure 11: Effect of Initial Concentration on Biosorption Capacity of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

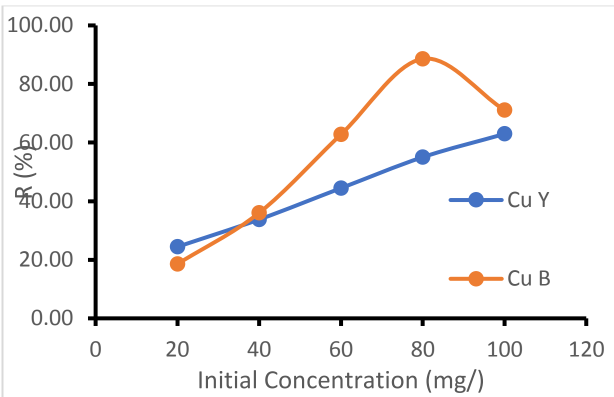

Figure 12: Effect of Initial Concentration on Removal Percentage of Copper onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Regarding copper ions, optimum biosorption capacity for copper ions onto *Bacillus circulans* (Cu B) and copper ions onto *Saccharomyces cerevisiae (Cu Y)* were observed at $100\ mg/l$ as observed in Figure 21 with value $3.56\ mg/g$ and $7.87\ mg/g$, respectively. The maximum percentage removal for copper ions onto *Bacillus circulans* (Cu B) and copper ions onto *Saccharomyces cerevisiae (Cu Y)* were measured at $80\ mg/l$ with value $88.58\ \%$ and at $100\ mg/l$ with value $62.94\ \%$ as displayed in Figure 22, respectively.

Based on the results recorded for effect of initial concentration of biosorbate the following can be made: The values of biosorption capacity increases with increase in initial concentration values for copper biosorbates. The percentage removal increases with increase in initial concentration from $20\ mg/l$ to $100\ mg/l$ for copper ions. This may be attributed to increase in concentration gradient with increase in initial concentration of biosorbate used as a driving force to minimise or eliminate mass transfer resistance between the aqueous biosorbate and the solid biosorbent. This can be explained by Jones *et al.* (2016), who reported that biosorption of $Cd^{2+}, Fe^{2+}, Ni^{2+}$ and Zn^{2+} onto Mucilage from *Dicerocaryum Eriocarpum* Plant as biosorbent increase with increase in the initial concentration of biosorbates. The results also agree with Kariuki *et al.* (2017), where biosorption of lead and copper ions using rogers mushroom biomass as biosorbent increase with increase in the initial concentration of each biosorbate.

Biosorption Isotherm and Kinetics Testing

Biosorption Isotherm

The results of biosorption isotherm testing for Langmuir isotherm model are presented in Figure 13 and the Langmuir model isotherm parameters are presented in Tables 1.

Langmuir isotherm model

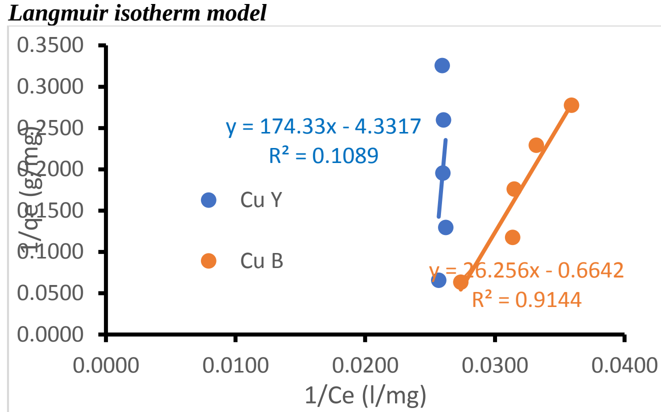

Figure 13: Langmuir Model Fitness for Copper ions onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Table 1: Langmuir Isotherm Model Parameters

Sample	q_{max} (mg/g)	K_L (l/mg)	R_L	R^2
Cu Y	-0.2308	-0.0248	-0.6757	0.1089
Cu B	-1.5056	-0.0253	-0.6536	0.9144

The Langmuir isotherm model gives maximum value of coefficient of determination (R^2) for copper ions onto *Bacillus circulans* $(Cu\ B)$ as 0.9144 and lowest value recorded as 0.1089 for copper ions onto *Saccharomyces cerevisiae* $(Cu\ Y)$ as shown in Table 1. The monolayer saturated capacity (q_{max}), Langmuir constant (K_L) and separation factor (R_L) give negative values for the two contacting processes which implies that the biosorption data do not give better fit of Langmuir isotherm model (Hossain, 2013; Kariuki *et al.*, 2017; Luka *et al.*, 2021).

Freundlich model

Figure 14 illustrated Freundlich isotherm model fitness testing and Freundlich model isotherm parameters are presented in Tables 2.

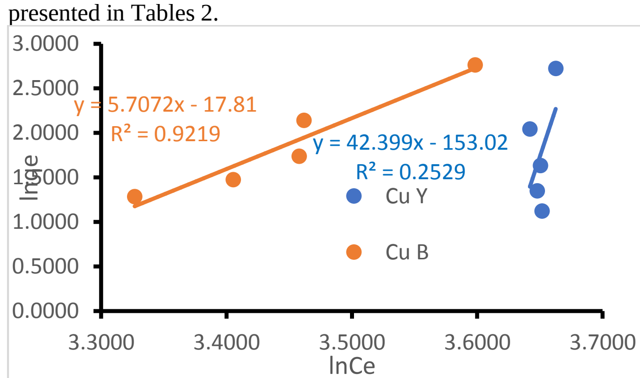

Figure 14: Freundlich Model Fitness for Copper ions onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Table 2: Freundlich Isotherm Model Parameters

Sample	1/n	n	K_F (mg/g l)	R^2
$Cu\ B$	5.7072	0.1752	1.84 X 10^{-8}	0.9219
$Cu\ Y$	42.399	0.0236	3.5 X 10^{-67}	0.2529

The Freundlich isotherm model parameters shown in Table 2 presented the coefficient of determination (R^2) for the biosorption of copper onto biosorbent with the maximum value recorded as 0.9219 for copper ions onto *Bacillus circulans*$(Cu\ B)$ and lowest value found as 0.2529 for copper ions onto *Saccharomyces cerevisiae* $(Cu\ Y)$. The values of intensity of heterogeneity ($\frac{1}{n}$) were recorded to be more than one (1) , which shows that the biosorption process is cooperative. Furthermore, values of intensity of biosorbate biosorption onto biosorbent (n) is less than one for all biosorption process which indicates biosorption of all biosorbate onto biosorbent are favourable. The equivalent maximum biosorption capacity for Freundlich constant (K_F) gives value measured in the ranged of $3.5\ X\ 10^{-67} - 1.84\ X\ 10^{-8}\ mg/g\ l$. The higher the value of K_F implies higher maximum biosorption capacity of biosorbate onto biosorbent. Therefore, Freundlich isotherm parameters are indicative of favourable fitness of Freundlich isotherm model for all biosorbate biosorption onto biosorbent (Hossain, 2013; Kariuki *et al.*, 2017; Verma *et al.*, 2017; Ahmad *et al.*, 2018; Luka *et al.*, 2021;).

Batch Biosorption kinetic models testing

Results of biosorption kinetic testing are presented in Figures 15 - 17.

Pseudo first order model

Pseudo first order model plots are given in Figures 15 and model parameters are shown in Table 3

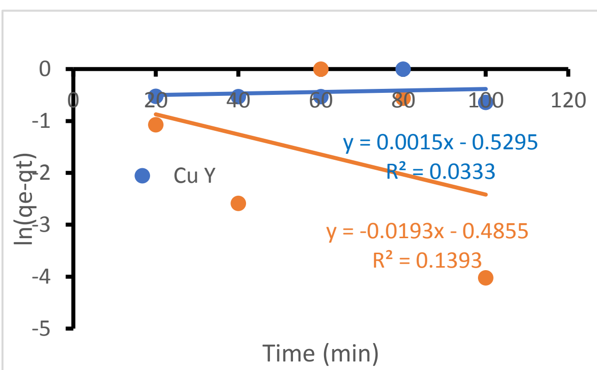

Figure 15: Pseudo first order Model Fit of Copper ions onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Table 3: Pseudo first order Model Parameters

Sample	K_1 (1/min)	q_e (mg/g)	R^2
$Cu\ Y$	-0.0015	2.1888	0.0333
$Cu\ B$	0.0193	2.233	0.1393

Figure 15 and Table 3 show that Pseudo first order Kinetics Model plots and Parameters obtained recorded lower values of coefficient of determination (R^2) and the experimental q_e values are not in agreement with the model's values for copper ions biosorption onto the different biosorbents tested. This is an indication that Pseudo first order Kinetics Model does not fit the data for biosorption of copper ions onto *Bacillus circulans* and *Saccharomyces cerevisiae* (Verma *et al.*, 2017; Ahmad *et al.*, 2018; Luka *et al.*, 2021).

Pseudo second order model

Pseudo second order model graphs are illustrated in Figure 16 and model parameters are presented in Table 4

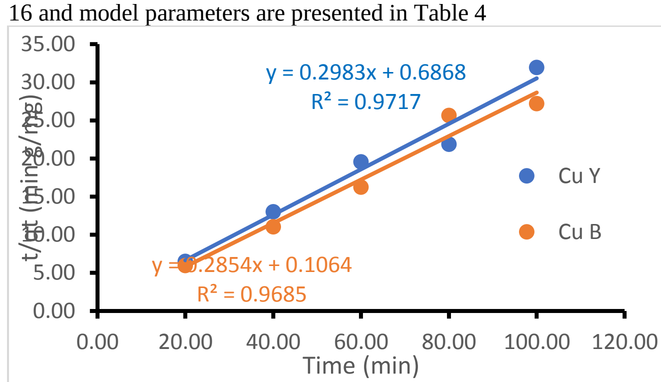

Figure 16: Pseudo second order Model Fit of Copper ions onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Table 4: Pseudo second order Model Parameters

Sample	K_2 (g/mg min)	q_e (mg/g)	h (mg/g min)	R^2
$Cu\ Y$	0.1297	3.35	1.4560	0.9717
$Cu\ B$	0.7655	3.50	9.3990	0.9685

The experimental values obtained were tested using Pseudo second order kinetics model and Parameters as depicted in Figure 16 and Table 4. Higher values of coefficient of determination (R^2) for all the biosorption carried out ranged from 0.9717 – 0.9685 were recorded and the experimental q_e values agree with the model's values for all analysis. The R^2 shows that *Bacillus circulans*$(Cu\ B)$ gives better fitness of Pseudo second order kinetics model to Saccharomyces *cerevisiae* $(Cu\ Y)$. This also indicate that copper ions onto different biosorbents used in this research agree with Pseudo second order kinetics model and the rate-limiting step may be chemisorption that involves valance forces through exchange or sharing of electrons (Hossain, 2013; Verma *et al.*, 2017; Ahmad *et al.*, 2018). The values of (K_2) which suggest the biosorption process in two reactions. The first one is the fast reaction, and equilibrium is attaining quickly while the second is slower reaction that can proceed for long time. The K_2 values for copper biosorption of biosorbent are less than one which indicate the mechanism is not chemisorption. The initial biosorption rate of copper (h) recorded the highest value as 9.3990 $mg/gmin$ for *Bacillus circulans* $(Cu\ B)$ with the lowest value found as 1.4560 $mg/gmin$ for Saccharomyces *cerevisiae* $(Cu\ Y)$.

Intra particle diffusion model

Intra particle diffusion model results are demonstrated in Figure 17 and model parameters are presented in Table 5.

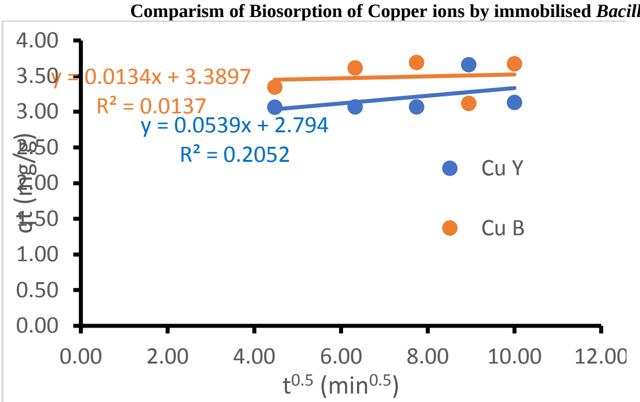

Figure 17: Intra particle Diffusion Model Fit of Copper ions onto *Bacillus Circulans* and *Saccharomyces Cerevisiae*

Table 5: Intra Particle Diffusion Model Parameters

Sample	K_{ip} (mg/g min$^{0.5}$)	C (mg/g)	R^2
Cu Y	0.0539	2.7940	0.2052
Cu B	0.0134	3.3897	0.0137

Furthermore, experimental results obtained from batch contactors were also tested for Intra particle diffusion kinetic model and parameters as presented in Figure 17 as well as Table 5. Figure 17 clearly observed that for copper biosorption onto different biosorbents investigated an intercept (C) was established. The values of intercept ranged from $2.7940 - 4.5870\ mg/g$ illustrating that the line does not pass through the origin and describing the boundary layer effects. Therefore, intra particle diffusion is not the rate controlling mechanism for biosorption (Amirnia, 2015; Nadeem *et al.*, 2016; Verma *et al.*, 2017; Luka *et al.*, 2021).

Conclusions

The following conclusions can be made from the results of this research:

1. *Bacillus circulans* and *Saccharomyces cerevisiae* biosorbents were able to remediate copper ions from wastewater; indicating suitability of both biosorbents for biosorption as depicted by Scanning electron microscope and Fourier transform infrared spectroscopy.
2. Immobilised *Bacillus circulans* gives better performance to *Saccharomyces cerevisiae* as biosorbents for the biosorption of copper ions from wastewater in a Batch process system.
3. Regarding batch contactor models, Freundlich isotherm model parameters are indicative of best fitness for copper biosorption onto the two different biosorbent examined. The kinetics obeyed Pseudo second order kinetics model with higher values of R^2 for all experimental data which ranged from $0.9717 - 0.9685$.

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