

Dead immobilized *Rhizopus Arrhizus* as a potential biosorbent for copper removal

Nadeem Feroze, Mohsin Kazmi[†], and Naveed Ramzan

Department of Chemical Engineering, University of Engineering & Technology, 54890, Lahore, Pakistan
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Abstract—The contemporary study reveals the potential of dead immobilized *Rhizopus Arrhizus* (DIRA) by studying the effects of initial pH of solution, contact time, initial Cu(II) concentration, co-ion, desorption and biosorbent reuse on the uptake of Cu(II) from synthetic solution. Optimum pH for Cu(II) biosorption on DIRA was 6.5. Pseudo second-order kinetic most suitably elucidated the kinetic trend. Removal of Cu(II) by DIRA followed the Freundlich adsorption isotherm. Experiments on effect of temperature revealed endothermic nature of Cu(II) biosorption upon DIRA. Na⁺ and Ca⁺ showed synergetic effect, while Mg⁺⁺ and Zn⁺⁺ revealed antagonistic effect on the biosorption of Cu(II). It was shown that reuse of DIRA was possible by means of 0.1 M HCl as an eluent.

Key words: Biosorption, Dead *Rhizopus Arrhizus*, Immobilization, Isotherm and Kinetic Models

INTRODUCTION

The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern, as the problem of removing pollutants from water and wastewater has grown with rapid industrialization. Heavy metals are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of afflictions [1,2].

Several methods such as chemical precipitation, ion exchange, membrane separation, and adsorption have been used for waste water treatment. A major drawback of precipitation technique is significant sludge production. Although ion exchange is considered to be a better alternative technique, it is expensive and the majority of ion exchangers do not have good selectivity to specified metal ions over other metal ions. Adsorption technique is considered to be among the most favorable processes because of its high efficiency and complete removal of metal ions even at low concentrations. The continuing increase in variety and amount of hazardous chemicals in effluents makes conventional adsorbents inefficient and sometimes even ineffective. Consequently, the development of new and more effective adsorbents has become essential, but at the same time it should be of low cost [3-9].

Due to the high costs of commercial adsorbents, biosorption is an economically feasible way to perform the treatment of potentially toxic species containing effluents. It is the sequestration of metals by the dead natural material called biosorbent. Among different biosorbents examined, the application of micro-organisms like algae, fungi and bacteria has been shown to be very promising [10-15]. They can be extracted from the environment or cultured in the lab. The cellular walls of biomass contain carboxylic acids, phenols, amine and amide groups which are responsible for heavy metals uptake [9,10].

Current investigation explores the potential of immobilized dead *Rhizopus Arrhizus* (R.A.). It was selected due to its non pathogenic

nature for humans and animals and it can be produced inexpensively whether through simple fermentation or as industrial waste from industrial fermentation processes such as lactic acid and lipase fermentation processes [15]. The objective of the existing work is to study the effects of pH, contact time, initial concentration, temperature, co-ion, desorption with HCl and reuse of DIRA on the uptake of Cu(II). Kinetic and equilibrium modeling was performed using classical models. R² was used to show the goodness of fit.

MATERIALS AND METHODS

1. Preparation of Dead Immobilized R.A. (DIRA)

Cells of DIRA were immobilized on a slab of reticulate polyurethane foam with the dimensions of 80×25×10 mm with 20 pores per linear inch. An L-shaped supporting stainless steel wire was used to place horizontally a pre-weighed slab of polyurethane foam at the bottom of 500 ml conical flask. These flasks sealed with cotton wool and covered with aluminum foil were autoclaved for 20 minutes. The growth medium containing glucose (30 g/L), yeast extract (10 g/L), malt extract (10 g/L) and double distilled water was prepared in a 2 liter flask, sealed with cotton wool and covered with aluminum foil on the top. The flask was then sterilized (autoclaved at 121 °C, 15 psig for 20 minutes) and left to cool. 100 ml of growth medium was poured into sterilized conical flasks containing reticulate polyurethane foam under aseptic conditions in a flow cabinet. A 0.5% V/V inoculum of spores suspension of *Rhizopus Arrhizus* was added by means of a micropipette to 100 ml liquid medium in each flask. The flasks were then incubated at 30 °C and 200 rpm in an orbital shaker for 48 hrs. The mycelia while growing in the bulk liquid got entrapped in the open pore network of the foam matrix, and at the end of growth almost all of the biomass was immobilized within the foam matrix. The medium was then decanted, washed twice with double distilled water and inactivated with 1% V/V formaldehyde to prepare the dead immobilized *Rhizopus Arrhizus* (DIRA) and stored until the biomass was needed for further experimentation.

2. Chemicals and Biosorption Studies

Copper stock solution was prepared by dissolving preweighed

[†]To whom correspondence should be addressed.
E-mail: engr.smalikazmi@gmail.com

quantity of analytical grade $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in double distilled water, and solution with desired concentrations were prepared by diluting the stock solution. Effect of pH was investigated between 2 and 7 using 100 ml analyte with 100 ppm copper concentration at $30 \pm 2^\circ\text{C}$ and 200 rpm and 80 minutes. For effect of contact time, 100 ml analyte with 30 ppm copper concentration was used. Samples were drawn at different intervals ranging from 5-80 minutes. Effect of initial copper concentration was studied between 2 to 100 ppm. Influence of temperature was observed between 5 to 40°C . Effect of co-ions (Na, Zn, Mg and Ca) on biosorption of Cu was examined keeping the concentration of each metal 15 ppm in a binary mixture. Kinetics of desorption of Cu from DIRA was investigated using 0.1 M HCl as an eluent. To study the reuse of the used DIRA, five samples of DIRA were first saturated with 10, 30, 50, 80, 100 ppm solutions. The loaded DIRA samples were then introduced to solution of different initial concentrations. Isotherm modeling was performed to explore the mechanism of biosorption. Residual metal concentration was determined using an atomic absorption spectrophotometer.

1 M KOH and 1 M HCl solutions were used to adjust the pH. Except for the pH study, 6.5 pH was used in all studies. For each experiment, immobilized biomass was thoroughly washed with double distilled water to discard any formaldehyde solution before biosorption experiments.

RESULTS AND DISCUSSION

1. Effect of pH

Biosorbent sites dissociation and solution chemistry are two important parameters which dictate the fate of the biosorption process and are highly influenced by pH [16,17]. During the course of biosorption many pH dependent interactions take place between the cell wall of the DIRA and Cu(II) solution. These include complexation, hydrolysis, redox reactions, precipitation etc [9]. Fig. 1 depicts the effect of initial pH on Cu(II) uptake by DIRA along with the final pH. It shows that increasing the initial pH of the solution, the uptake of Cu(II) by DIRA increases. The trend has three distinct regions: a linear increasing trend between pH 2-5, a relatively flat region between pH 5-6, and an increasing portion beyond pH 6. This pattern has been shown earlier [16] and explained as at lower pH the functional groups of DIRA responsible for uptake of Cu(II) are surrounded by H_3O^+ . Due to electrostatic repulsion of H_3O^+ and

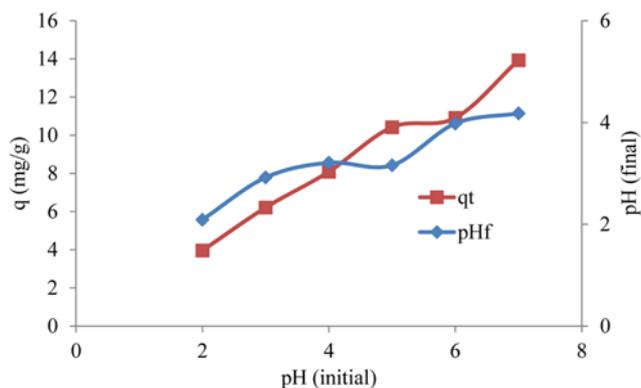


Fig. 1. Effect of initial solution pH on Cu(II) uptake and final solution pH.

Cu^{++} a lower uptake has been observed at the lower end of pH curve [7,9,17]. Since the uptake of Cu(II) is not zero even at the lowest pH tested in this work, it can be concluded that removal of Cu(II) from the solution is governed by multiple mechanisms acting side by side. At greater pH, functional groups of the biomass are negatively charged and there is less hindrance of H_3O^+ , which results in higher uptake of Cu(II) [9]. Fungi of each group have distinct composition and structure of the cell wall. However, it has been found that two basic of binding compounds may be identified in each type: glucosamines (Chitin-chitosan unit, proteins and amino acids) and ionizable binding groups (phosphate and carbonyl groups of uronic acids) [15].

Another important feature of the pH study is the value of the final pH. It was measured and is shown in Fig. 1. Overall, the pH of the solution decreased during the course of biosorption of Cu(II) onto DIRA. This was probably due to the release of protons from the DIRA, indicating the possibility of Cu(II) removal through ion exchange mechanism [18]. The pH study was not performed beyond $\text{pH} > 7$ to avoid precipitation. pH 6.5 was taken as optimum pH to study various other parameters like contact time, initial concentration and temperature.

2. Effect of Contact Time

Time course of a metal biosorption strongly depends on the nature of biosorbent. Passive removal of metal by dead biomass is independent of its metabolism and attains equilibrium in less than 15 minutes for mesophilic organisms [19]. However, in the current study more than 90% (2.67 mg/g) of the equilibrium uptake (2.96 mg/g) was achieved within ten minutes as shown in Fig. 2. Similar results have been reported elsewhere [7]. Biosorption of Cu(II) onto DIRA involves multiple steps as can be seen in Fig. 2. Initial rapid step is attributed to the removal of the Cu(II) by the vacant binding sites present on the surface of DIRA followed by a slower step indicating intraparticle diffusion [20]. Equilibrium was achieved in 60 minutes as no improvement in uptake was observed after this length of contact time.

2-1. Kinetic Modeling

Biosorption kinetics was simulated through Elovich, pseudo 1st order and pseudo 2nd order kinetics. Elovich and pseudo 1st order kinetics showed poor correlation coefficients indicating inapplicability of them on the biosorption of Cu(II) onto DIRA. Linearized form of pseudo 2nd kinetic is defined by the following equation [8]:

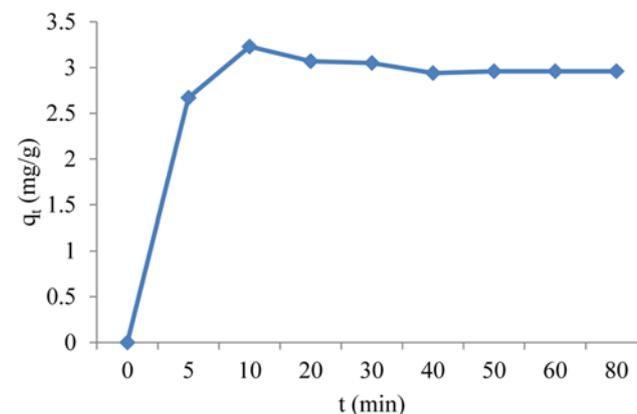


Fig. 2. Effect of contact time on the uptake of Cu(II) DIRA.

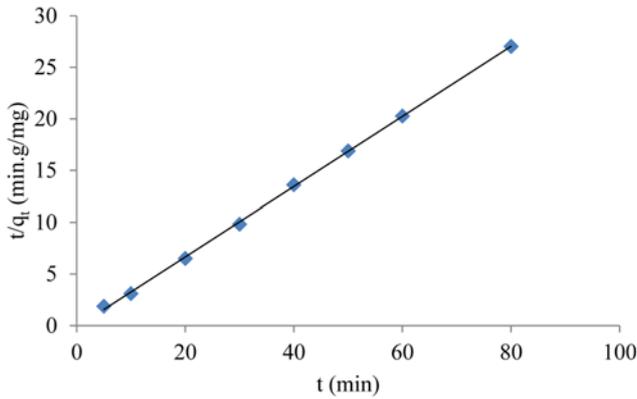


Fig. 3. Pseudo 2nd order kinetics for Cu(II) uptake onto DIRA.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (1)$$

This relation is based on the concept that biosorption uptake is directly proportional to the amount of binding sites engaged by the metal ions and that chemisorption is the rate controlling step. A plot between t/q_t and t is shown in Fig. 3. q_e (2.94 mg/g) calculated from the slope of the graph was in close agreement with the experimentally observed $q_{e,exp}$ (2.96 mg/g), indicating an excellent fitting ($R^2=0.9996$) of this model to the kinetic data.

To find rate the controlling step, a simple model of Weber and Morris was applied as given by the following equation [20]:

$$q_t = k_d t^{0.5} + C \quad (2)$$

If the plot between q_t and $t^{0.5}$ shows a straight line, then the rate controlling step is intraparticle diffusion. However, the plot in Fig. 4 shows multi-linearity, indicating that the rate controlling step is not the intraparticle diffusion. It may be concluded that Cu(II) onto DIRA is due to chemisorption, which also limits the rate of biosorption.

3. Effect of Initial Concentration

Study of initial concentration facilitates the determination of performance of a biosorbent under a variety of mass transfer driving forces. To do so a series of experiments were performed in which solutions with different initial Cu(II) concentrations were contacted with DIRA as shown in Fig. 5 through a plot between q_e Vs C_e . Similar pattern has been observed in previous studies for biosorption of Cu(II) onto dead biomasses [7]. The uptake of Cu(II) onto DIRA

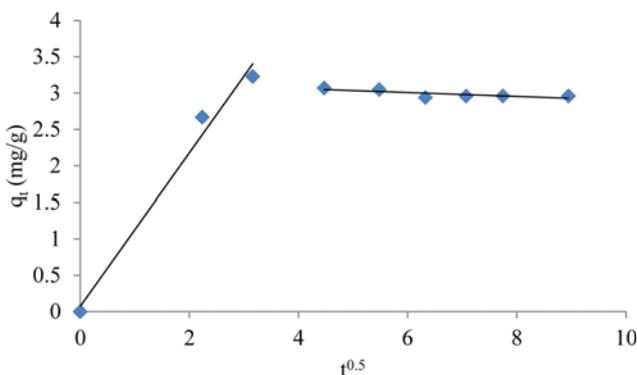


Fig. 4. Pore diffusion model for Cu(II) biosorption onto DIRA.

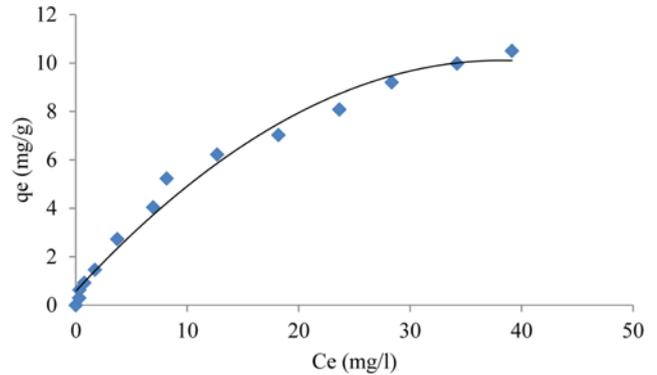


Fig. 5. Effect of initial concentration of Cu(II) on uptake by DIRA.

increased from 0.924 mg/g to 10.503 mg/g when initial concentration was increased from 2 to 100 mg/l. This is because as the initial concentration increased more and more, vacant binding sites were occupied by the Cu(II) resulting in an increase in the uptake.

3-1. Equilibrium Modeling

To unveil the possible mechanism, two frequently employed isotherms, namely Langmuir and Freundlich models, were employed. An isotherm represents the relationship of a metal distributed between two phases (solid and liquid) at equilibrium. Generally used isotherms are empirical relations developed based on certain assumptions. Their application facilitates a quick evaluation of not only mechanism but also helps to compare the performance of one biosorbent with other.

The Langmuir isotherm is based on the simple assumption that all the binding sites are similar and metal rests upon the biomass surface in a monolayer. A linearized form of the Langmuir isotherm is as follows [6]:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}} \quad (3)$$

q_{max} and b are Langmuir constants and represent maximum biosorption capacity and affinity of a biosorbent for adsorbate. These parameters are calculated from the slope and intercept of a graph between C_e/q_e versus C_e as shown in Fig. 6. Values of q_{max} and b

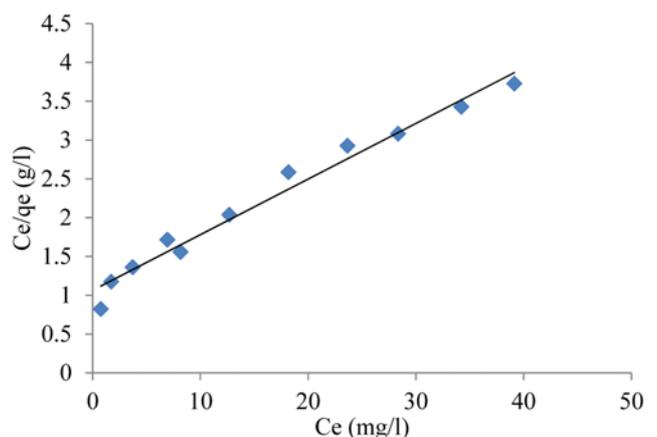


Fig. 6. Application of Langmuir model for Cu(II) biosorption on DIRA.

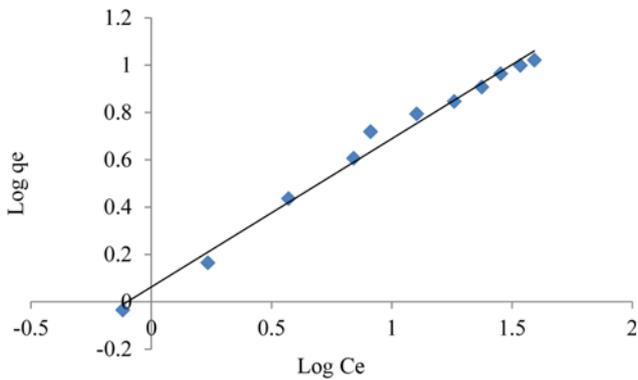


Fig. 7. Application of Freundlich model for Cu(II) biosorption on DIRA.

were 13.95 mg/g and 0.0674, respectively. The Langmuir model showed fairly good fitting to the data as goodness of fit R^2 , the coefficient of correlation, was 0.9762. This showed the possibility of the removal of Cu(II) by DIRA in the form of a single layer. Since the R^2 was not unity, there was a need to search for a better description of the process.

Contrary to the Langmuir model, the Freundlich model is based on the binding sites heterogeneity and can be written in the following linearized form [1]:

$$\log q_e = \log K_f + \frac{\log C_e}{n} \tag{4}$$

K_f and n are Freundlich constants and can be calculated from the slope and intercept of a graph between $\log q_e$ and $\log C_e$ as shown in Fig. 7. K_f and n were 1.16 and 1.57, respectively. The value of correlation coefficient was 0.9883, which showed that the Freundlich model described the Cu(II) biosorption onto DIRA better than did the Langmuir. This is in agreement with the fact of multiple binding sites (carboxylic, amines, carbonyl and phosphate groups) as discussed earlier in the section 1. A comparison of performance of DIRA with past studies is given in Table 1.

4. Effect of Temperature

Fig. 8 shows the effect of temperature on the biosorption of Cu(II) onto DIRA. It can be seen that effect of temperature is relatively less on the uptake as compare to pH. However, an increase in uptake can be observed with increase in temperature. This indicates that the process of Cu(II) removal by DIRA was endothermic. A number of reasons may be associated with the increase in uptake: (1) Increase in number of active sites due to bond rupture at higher temperature, (2) Increase in kinetic energy of the metal ion resulting in ease of approach of Cu(II) to binding sites of DIRA, (3) Ease in attaining the activation energy resulting in formation of stable com-

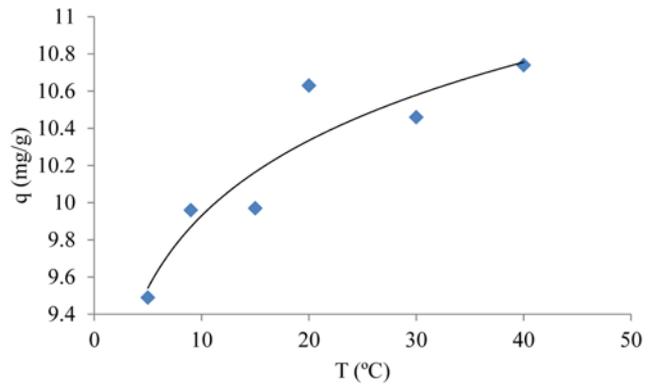


Fig. 8. Effect of solution temperature on the uptake of Cu(II) on DIRA.

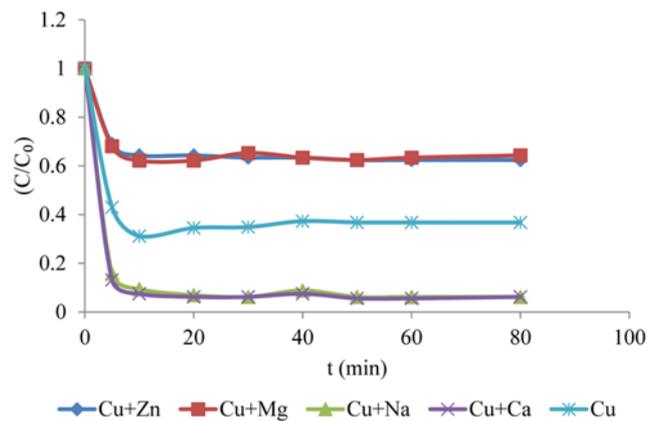


Fig. 9. Effect of co-ion on uptake of Cu(II) on DIRA.

plexes, and (4) widening of pores hence facilitating the pore diffusion [19,24-26]. Since the process of biosorption of Cu(II) onto DIRA is complex, as pointed out in section 3.1, so a combination of aforementioned mechanisms may be there to promote the uptake of Cu(II) onto DIRA. Since the increase in uptake from 5 to 40 °C was just 1.25 mg/g, it may be thought that biosorption of Cu(II) onto DIRA mainly occurred by some energy-independent mechanisms.

5. Effect of Co-ion

Effect of co-ion is important to study as in real wastewater multiple ions are present, which may represent antagonism or synergism. Fig. 9 depicts a kinetic comparison of copper(II) concentration profiles for different binary systems with copper(II) single component. It can be observed that relative concentration (C/C_0) is significantly affected by the co-ion. It shows that equilibrium time was unaffected by the type of metal ion present and it remained 60 minutes. However, the ratio of C/C_0 was higher at equilibrium for Cu+Zn

Table 1. Comparison of DIRA with previous studies

Sr.#	Biosorbent-metal	State (free/immobilized)	Adsorption capacity (mg/g)	Adsorption type	Reference
1	Rhizopus Arrhizus-Cu	Free	33.8	Freundlich	[21]
2	Rhizopus Arrhizus-Zn	Free	12.78	Freundlich	[21]
3	Rhizopus Arrhizus-Pb	Free	56.5	Langmuir	[22]
4	Rhizopus Arrhizus-Cu	Immobilized	13.95	Freundlich	This study
5	Rhizopus Arrhizus-Cr(VI)	Immobilized	9.85	Freundlich	[23]

and Cu+Mg systems as compared to single component (Cu only) as well as Cu+Na and Cu+Ca. Presence of Zn and Mg indicated antagonistic effect as the equilibrium concentrations of Cu(II) in binary solutions were greater than single Cu(II) system, representing lower removal of Cu(II) [3,27]. It can be interpreted as, Zn and Mg competed with Cu to occupy the available sites which resulted in lowering of Cu uptake. Na and Ca exhibited synergetic effect as the residual Cu(II) concentration in binary systems (Ca+Cu, Na+Cu) at equilibrium time was lower than Cu(II) mono component. This could be explained as the presence of Na and Ca catalyzed the sorption of Cu(II), as a result of which Cu(II) was removed in higher magnitude giving lower relative concentration (C/C_0) of Cu(II) at equilibrium [3,27].

6. Desorption and Reuse

The reuse of a metal loaded biomass upon regeneration is an attractive feature of the biosorption process. Metal ion may desorb when contacted with suitable acidic or basic eluent. In this work 0.1 M HCl was used as regenerating media. Usually, regeneration does not result in 100% removal of metal from the biosorbent [28]. The amount of metal retained on the biosorbent increases as the number of regenerations increases. Fig. 10 shows the effect of contact time on % desorption of Cu(II) from DIRA. It shows that desorption takes place in multiple steps. The maximum % desorption achieved was 62.81%. Cu(II) desorption from DIRA was fastest in first ten minutes, which counted for approximately 96% of total desorption [28]. Increasing contact time for desorption from 10 to 60 minutes resulted in an increase of % desorption from 60.49% to 62.71%, representing an increment of just 3.5%. Equilibrium was established at 90 minutes as % desorption did not increase beyond this time. It can be interpreted as that in first 10 minutes the removal of Cu(II) was from the surface of the DIRA due to which an abrupt recovery of Cu(II) was observed. After this, Cu(II) adsorbed in the DIRA due to intraparticle diffusion was recovered. Hence, desorption supported the study of effect of contact time. Equilibrium time for desorption was taken as 90 minutes. It is important to observe that around 37% Cu(II) did not desorb from DIRA and remained on it. This feature was used to perform another series of experiments to study the extent of regeneration on the reuse of DIRA through equilibrium isotherm.

Five samples of loaded DIRA were prepared by contacting with 10 mg/l, 30 mg/l, 50 mg/l, 80 mg/l and 100 mg/l solutions of Cu(II) separately for equilibrium time. The corresponding equilibrium up-

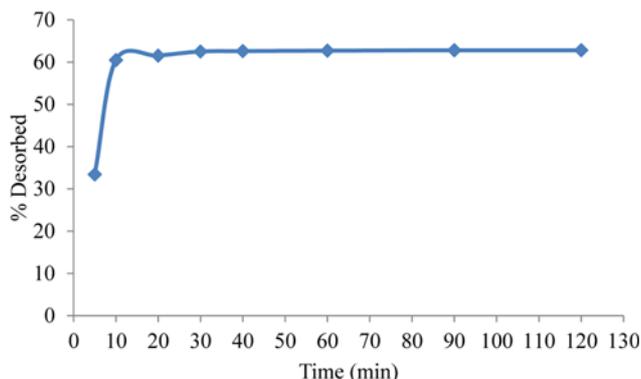


Fig. 10. Effect of contact time on desorption of Cu(II) on DIRA.

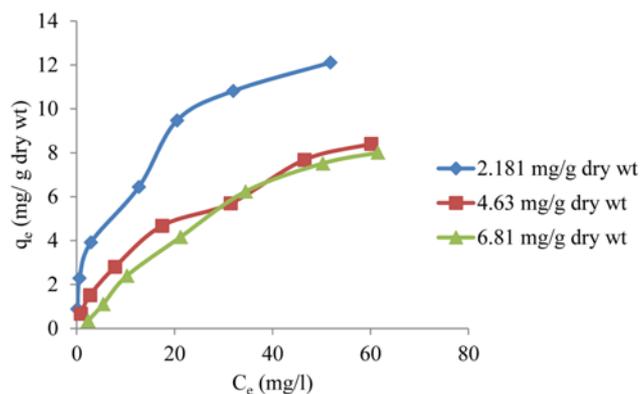


Fig. 11. Effect of initial Cu(II) concentration on uptake by Cu(II)-loaded DIRA.

takes of Cu(II) by loaded DIRA samples were 2.181 mg/g dry wt., 4.63 mg/g dry wt., 6.81 mg/g dry wt., 7.67 mg/g dry wt. and 9.066 mg/g dry wt., respectively which were assumed as the amounts of Cu(II) left on DIRA after various regeneration cycles. These loaded samples were used for the study of the effect of initial concentration of Cu(II) as shown in Fig. 11. It illustrates the effect of initial concentration for 2.181 mg/g dry wt., 4.63 mg/g dry wt. and 6.81 mg/g dry wt only. As a matter of fact, a negative value of equilibrium concentrations was obtained for loaded DIRA samples with initial uptakes higher than 6.81 mg/g dry wt. It indicated that the loaded DIRA samples with higher initial uptake were not only unable to hold additional Cu(II) due to occupation of all sites, but also desorption of Cu(II) took place from them. For the given equilibrium concentration the uptake of the DIRA sample corresponding to an initial uptake of 2.181 mg/g dry wt. was higher than those of 4.63 mg/g dry wt. and 6.81 mg/g dry wt. as shown in Fig. 11. Similarly, the uptake by DIRA sample corresponding to initial uptake of 4.63 mg/g dry wt was higher than that corresponding to 6.81 mg/g dry wt. This trend can be interpreted as sample having less initial uptake of Cu(II) had relatively more un-occupied sites as compared to the loaded DIRA with higher Cu(II). Thus, a curve with higher uptake was observed for DIRA samples with lower initial uptake.

Equilibrium modeling was performed for the effect of initial concentration on reuse of DIRA. The R^2 values for runs corresponding to samples having initial loadings 2.181 mg/g dry wt., 4.63 mg/g dry wt. and 6.81 mg/g dry wt. were 0.9644, 0.9584 and 0.4224 for

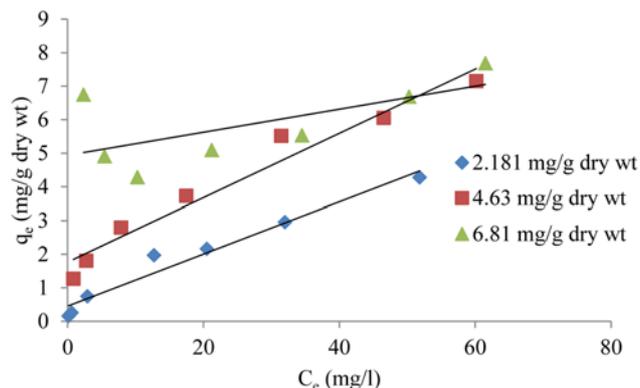


Fig. 12. Application of Langmuir model for Cu(II)-loaded DIRA.

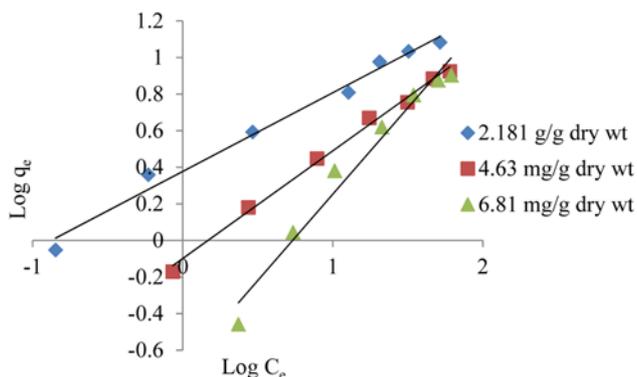


Fig. 13. Application of Freundlich model for Cu(II)-loaded DIRA.

Langmuir and 0.9856, 0.9952 and 0.9713 for Freundlich isotherm, respectively. As expected, the curve for each initial uptake was better satisfied by the Freundlich isotherm than Langmuir as shown in Fig. 12 and 13.

CONCLUSIONS

Following conclusions were drawn:

1. Highest uptake of Cu(II) onto DIRA takes place at pH 6.5, which was used in the study of other factors. Decrease of pH at the end of experiments suggested ion exchange mechanism.
2. Equilibrium time for Cu(II) biosorption onto DIRA was 60 minutes and pseudo 2nd order kinetic model enumerated best.
3. Study of Cu(II) uptake at various initial concentrations indicated promising % removal. Both Langmuir and Freundlich models showed a higher value of correlation coefficients: >0.9500. Application of Freundlich isotherm was validated due to the existence of multiple binding sites.
4. Temperature showed minor influence on the uptake of Cu(II) between 5 to 40 °C. However, slight increase of uptake indicated endothermic nature of Cu(II) biosorption onto DIRA.
5. Binary mixtures study with Na, Ca, Mg and Zn revealed, Na and Ca have catalyzing effect on uptake of Cu(II) by DIRA and Mg and Zn have inhibitory effect.
6. Maximum desorption did not exceed 62.81% upon extension of contact time of eluent (0.1 M HCl) to the loaded DIRA from 90 to 120 minutes. Desorption equilibrium was reached in 90 minutes. DIRA with lower initial uptake showed higher binding of Cu(II) when studied against various initial concentrations. Beyond initial uptake of 6.81 mg/g dry wt., instead of uptake Cu(II) desorbed from the DIRA. Freundlich isotherm showed better R² than Langmuir to model reuse of DIRA.

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