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Biosorption of Mg(II) from water by *Rhizopus arrhizus*

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ABSTRACT

The current research was performed on dead and immobilized *Rhizopus arrhizus* (D.I.R.a.), in order to remove Mg(II) from water; this includes the effects of pH, contact time, initial dye concentration, temperature, and co-ions. It was observed that the optimum pH for the process was 6.5. The extent of removal was enhanced with an increase in contact time and initial concentration. The uptake of Mg(II) onto D.I.R.a. grew rapidly, from 0.705 to 7.13 mg/g, when the initial concentration was raised from 2 to 100 mg/L. Kinetic and equilibrium studies revealed that equilibrium was achieved within 60 min. Sorption isotherm studies showed that Freundlich isotherm model is applicable, and the values of R^2, K_f, and n were 0.987, 0.74, and 1.62, respectively. The experiments on co-ions revealed that the presence of Cu(II) ions inhibits the uptake of Mg(II) by D.I.R.a.

Keywords: Biosorption; *Rhizopus arrhizus*; Kinetic and equilibrium modeling

1. Introduction

A significant fraction of the human body is made up of water both by weight and volume and it is the most consumed liquid in the world. Water contains various types of minerals, which are classified into two categories: macro (K, Ca, Na, and Mg) and micro (Zn, Fe, and Cu) minerals. Although these minerals are vital for one's health, they can be lethal in high concentrations. It is therefore necessary to consume an adequate amount of the essential mineral nutrients to avoid biological complications [1]. To meet the consumer demands, industries have implemented various advanced technical processes to clean water.

Mg(II) is fourth on the list for cation concentrations in the body and second on the list for intracellular fluids. It is a contributing factor of approximately 350 cellular enzymes; numerous of which participate in metabolic process. It is involved in nucleic acid and protein unit production and is compulsory for the functioning of insulin sensitivity and normal vascular tone [2]. Mg(II) is essential to human life, provided it is in a specific quantity. The United States Food and Nutrition board of the Institute of Medicine (FNB/IOM) has published the recommended dietary allowance (RDA) in the form of average daily intake that fulfills the nutrition demand closely for all healthy individuals in a particular stage of life and gender; for males, the quantity is 420 mg/d and for females, 320 mg/d [1]. Inadequate doses of magnesium can result in the deterioration of health.

Magnesium, though not lethal, can cause health issues when quantities greater than the suggested dose are consumed, a few being; problems with gastrointestinal function, nausea and vomiting, lethargy, muscle weakness, irregular heartbeat, low blood pressure, urine retention, respiratory distress, and cardiac arrest [2,3]. Magnesium has a lot of different sources and as a result may end up in water through various ways. Chemical industries add magnesium to plastics and other materials either as a measure against fire or as filler. It also ends up in the environment from fertilizers

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and from cattle feed. Magnesium sulfate is used in beer breweries; magnesium hydroxide is applied as a flocculent in wastewater treatment plants. Magnesium alloys are utilized in the construction of car and plane bodies. Several quantitative analytical methods have been developed for magnesium. The most commonly implemented techniques listed are; ion exchange, mass spectrometry, distillation, membrane separation, reverses osmosis, inductively coupled plasma mass spectrometer, filtration, and atomic absorption spectrophotometry [1,2,4].

Biosorption is the removal of pollutants by dead biomaterial [5–8]. It is considered as an economical alternative for remove of heavy metals from dilute solution (concentration < 100 ppm) [5]. It shows fast kinetics to achieve a suitable removal of heavy metals. Removal of a pollutant (heavy metal or organic compound) by biosorption is greatly affected by the presence of a co-ion. Calcium and magnesium naturally exist in water along with other alkali metals. It has been observed that magnesium adversely affects the removal of other pollutants such as heavy metals [9]. However, Mg(II) has not been given much attention and very few researchers have worked on its removal [10–14].

In our previous studies, we have reported that *Rhizopus arrhizus* has great potential for the removal of Cu(II) and Zn(II). As there are very few studies on the biosorption of Mg(II). Therefore, the basic aim of this work is to study the biosorption of Mg(II) by dead and immobilized *Rhizopus arrhizus* (D.I.R.a.). In this study, important parameters, such as the effect of pH, co-ions, contact time, initial dye concentration, temperature and co-ions on the biosorption of Mg(II) are investigated. Kinetic and equilibrium modeling are performed using classical models. R^2 is used to show the decency of the fit.

2. Materials and methods

2.1. Development of dead and immobilized Rhizopus arrhizus

Procedure for the development of D.I.R.a. was adopted as described by Ileri [15]. Cells of *R. arrhizus* were immobilized on a slab of polyurethane foam of dimensions 80 × 25 × 10 mm with a mesh number of 20. An L-shaped supporting stainless steel wire was used to horizontally place the slab of polyurethane foam at the bottom of a 500 mL conical flask. These flasks secured with cotton wool and concealed with aluminum foil were autoclaved for 20 min. The growth medium, containing glucose (30 g/L), yeast extract (10 g/L), malt extract (10 g/L), and double distilled water were prepared in a 2-L flask, covered with cotton wool and aluminum foil on the top. The flask was then sterilized (autoclaved at 121°C, 15 psig for 20 min) and left to cool. 100 mL of the growth medium was poured into sterilized conical flasks containing convolute polyurethane foam under clean conditions in a flow cabinet.

0.5% V/V inoculums of spore suspensions of *R. arrhizus* were added by means of a micropipette to a 100 mL liquid medium in each flask. The flasks were then incubated at 300°C and 200 rpm in an orbital shaker for about 48 h. The mycelia, growing in the bulk liquid, were entrained in the open pore network of the foam matrix, and at the end of growth, all the biomass was immobilized within the foam matrix. The medium was then drafted, washed twice with double distilled water and inactivated with 1% V/V formaldehyde to prepare the D.I.R.a. and stored until the biomass was needed for further experimentation and tests.

2.2. Chemicals and biosorption studies

The magnesium stock solution was prepared by dissolving the predetermined quantity of analytical grade magnesium nitrate, attached chemically with three molecules of water of crystallization in duplex refined water; solutions of desired concentrations were prepared by diluting the standard solution. The effect of pH was considered between values of 2 and 7 when using an analyte volume of 100 mL, with the magnesium concentration of 100 ppm at a temperature 30°C ± 2°C, at 200 rpm and a contact time of 80 min. To study the effect of contact time, 100 mL analyte with a magnesium concentration of 30 ppm was used. Samples were taken out at different intervals between 5 and 80 min. Effect of initial copper concentration was studied between 2 and 100 ppm. Impact of temperature was observed to be between 5°C and 40°C. Effect of co-ions (Mg, Cu + Mg) on biosorption of Mg(II) was examined, keeping the concentration of each metal to 15 ppm in a binary mixture. Kinetics of desorption of Mg(II) from D.I.R.a. was investigated using 0.1 M HCl as an eloquent. To study the reuse of the used D.I.R.a., five samples of D.I.R.a. were saturated with 10, 30, 50, 80, and 100 ppm solutions. The available D.I.R.a. samples were then raised to a solution of different initial concentration. Isotherm modeling was performed to judge the internal structure of biosorption. Unconsumed metal concentration was deduced using an atomic absorption spectrophotometer. 1 M KOH and 1 M HCl solutions were used to maintain the pH. In addition to all of the above, a pH of 6.5 was used in the testing of all samples. For each experiment, immobilized biomass was thoroughly scrubbed with double distilled water to eliminate any formaldehyde before the biosorption experiments.

3. Results and discussion

3.1. Effect of pH

The segregation of active reactant sites and the composition of the solution are two substantial properties, which actually decide the completion of the biosorption process; the two are highly affected by the pH as well [16,17]. During the operation of biosorption, many complex chemical reactions come into play between the cell wall of the D.I.R.a. and the magnesium nitrate solution, which may or may not be related to the pH. These reactions comprise mainly of complicated ion dissociations, reduction oxidation reactions, hydrolysis, adsorption, precipitation, etc. [18]. Fig. 1 depicts the dependency of Mg(II) uptake the initial pH by the D.I.R.a. along with the final pH. It shows the direct relation between the pH value and Mg(II) uptake with the help of the D.I.R.a. The trend has three definite domains, a steady state increase between pH 2 and 5, decreasing between pH 5 and 6, and a rapid increase after reaching a pH of 6. This pattern has also been shown at an initial stage as well and this was the reason why we had the idea that at a lower value of pH, the functional groups of D.I.R.a. are hindered in the uptake of Mg(II) molecules, which are surrounded by the hydronium ions [16]. Due to the electrostatic reclusion of H_3O^+ and Mg^{++}, a lower uptake has been noticed at the bottom of the pH curve [17–19]. As the uptake of Mg(II) is not zero or minimum even at the lowest value of pH, from this observation, it can be reasoned that the elimination of Mg(II) from the solution is controlled by diversified form of mechanisms. At a high value of pH, the functional groups of the biomass are negatively charged providing a platform of less restriction against H_3O^+, which results in a greater accommodation of Mg(II) [7]. Commonly, the binding compounds in fungi are glucosamine (chitin–chitosan unit, proteins and amino acids) and ionizable binding groups (phosphate and carbonyl groups of uronic acids) [20].

The other side of pH analysis is the value of the final pH. It was evaluated and is shown in Fig. 1. In summary, the pH of the solution or a given sample decreased during the attack of biosorption of Mg(II) onto D.I.R.a. This might be conditionally due to the liberty of protons from the D.I.R.a., pointing out the possibility of Mg(II) removal through an ion-exchange medium. The pH analysis was not carried out beyond pH> 7 to avoid precipitation. The optimum value of pH 6.5 was chosen to study the other different parameters such as reaction or contact time, initial concentration, and temperature.

3.2. Effect of contact time

Time period of the metal biosorption firmly depends upon the nature and composition of the biosorptive material. Uptake of metals by dead biomass has no dependency on its metabolism and has the capability to attain steady state in less than 15 min, for mesophilic organisms [21]. However in our study, more than 90% (2.97 mg/g) of the equilibrium was achieved within 10 min as shown in Fig. 2(a). Similar results have been derived elsewhere as well [19]. Biosorption of Mg(II) onto D.I.R.a. mainly involves two basic steps as indicated by Fig. 2(a). The initial active step is featured by the removal of Mg(II) by the vacant binding active sites present on the surface of D.I.R.a., followed by the rate-determining step, indicated by the diffusion between the layers of the particles [22]. Equilibrium was achieved within 60 min and no significant modification in the uptake was observed after this period of contact time.

3.2.1. Kinetic modeling

Biosorption kinetics was simulated through the Elovich, pseudo-first-order and pseudo-second-order kinetics. The Elovich and first-order models showed poor correlation coefficients, indicating their unsuitability regarding the biosorption of Mg(II) onto D.I.R.a.

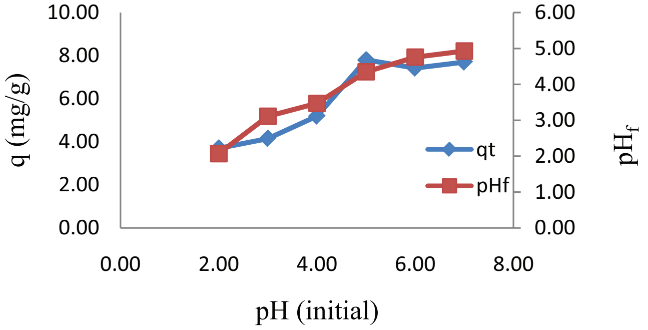

Fig. 1. Effect of initial solution pH on Mg(II) uptake and the final pH of solution.

Linearized correlation form of pseudo-second-order kinetics can be expressed as follows [23]:

$$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{K_2q_e^2} \tag{1}$$

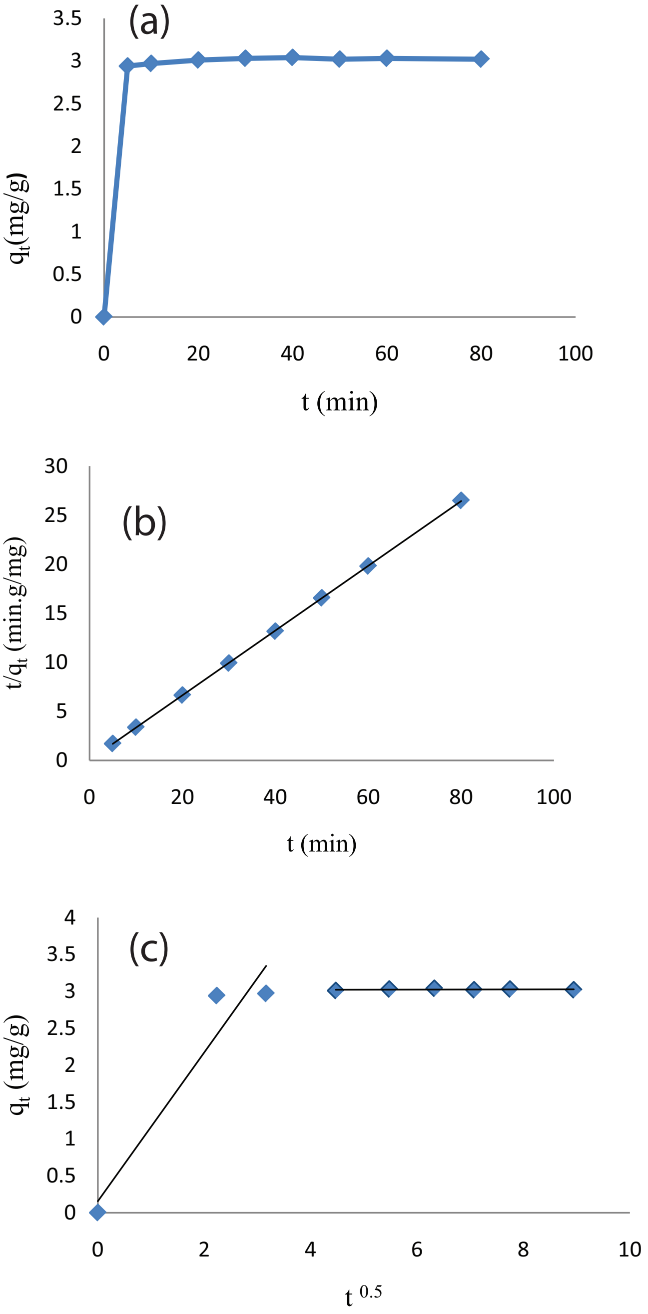

Fig. 2. (a) Effect of contact time on the uptake of Mg(II) onto the dead and immobilized *Rhizopus arrhizus*. (b) Pseudo-second-order kinetics for Mg(II) uptake on the dead and immobilized *Rhizopus arrhizus*. (c) Pore diffusion model for Mg(II) biosorption onto the dead and immobilized *Rhizopus arrhizus*.

where q_e is the uptake at equilibrium, q_t is the uptake at any time and K_2 is the pseudo-second-order rate constant. The above equation gives us a clear idea that biosorption uptake is directly proportional to the magnitude of the active reactant sites accompanied by the metal ions. A relationship between t/q_t and t is shown in Fig. 2(b). q_e (3.03 mg/g), calculated from the slope of the graph was in close harmony with the experimentally observed q_e (3.02 mg/g), displaying an excellent fitting ($R^2 = 1.000$) of this model to the kinetic data.

Uptake of a metal ion from solution on biosorbent involves multiple steps. Literature shows that biosorption proceeds in two major steps, that is, external mass transfer (boundary layer diffusion) and interparticle diffusion. To work out the rate-determining step, a simple and easy model of Weber and Morris was applicable, which is given by the following equation [22]:

$$q_t = K_{\mathrm{id}} t^{0.5} + C \tag{2}$$

According to the equation, if the plot of the graph between q_t vs. $t^{0.5}$ shows a linear relation, then the rate-controlling step is the intraparticle diffusion, but according to the graphical plot in Fig. 2(c), a mosaic-linearity is shown, illustrating that the rate-controlling step is not the intraparticle diffusion.

Thus, it could be concluded that instead of interparticle diffusion, film diffusion may be the rate-controlling step [22].

3.3. Effect of initial concentration

Comprehensive analysis of the initial concentration depicts the ability of a biosorbent to work under different categories of mass transfer driving forces. To fulfill this criterion, a number of experiments were executed in which solutions with variant initial Mg concentrations were brought in contact with D.I.R.a. as shown in Fig. 3(a) through the setup between q_e vs. C_e. An identical model has been inspected in the previous studies for the biosorption of Mg(II) onto the dead biomass [19]. The uptake of Mg(II) onto the D.I.R.a. showed a rapid rise, from 0.705 to 7.13 mg/g, when the initial concentration was upgraded from 2 to 100 mg/L. The trend is observed due the Mg(II) occupying the vacant binding sites, resulting in an increase in the uptake.

3.3.1. Equilibrium modeling

Two famous and repeatedly developed isotherms, namely Langmuir and Freundlich models, were chosen to deduce the possible mechanism. An isotherm imitates the affinity of a metal, distributed between two states of matter (solid and liquid) at a steady state. Usually, isotherms are pragmatic relations obtained by taking certain assumptions. Their usage assists in the progress of a quick and fast appraisal of not only the mechanism, but also helps in the comparison of one biosorbent performance to the other.

The Langmuir isotherm is established on the simple conjecture that all the binding sites are identical and the metal rests upon the biomass within a thin solitary layer. A linearized form of the Langmuir isotherm is as follows [24]:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \tag{3}$$

In the above equation $q_{\max}$ and b are Langmuir constants and represent maximum biosorption retention, also highlighting the compatibility of a biosorbents and the adsorbate. C_e and q_e are the concentration and uptake at equilibrium, respectively. These specifications are estimated from the

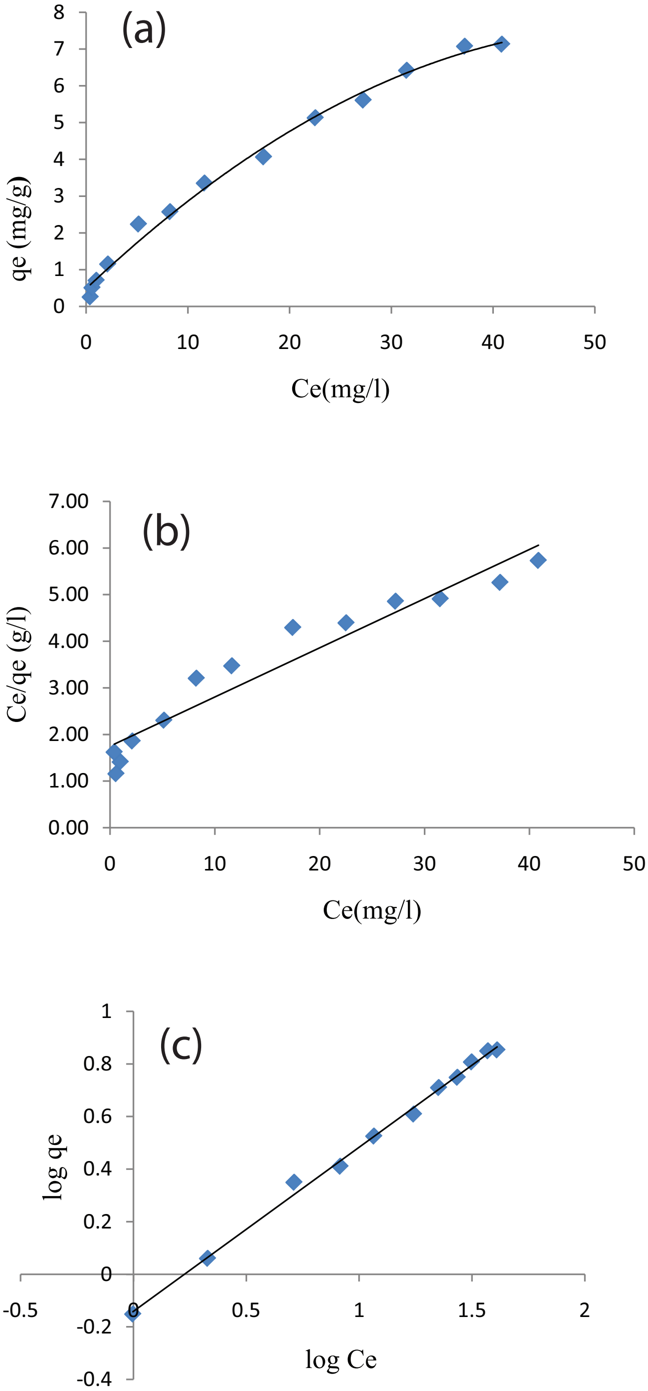

Fig. 3. (a) Effect of initial concentration of Mg(II) on uptake by the dead and immobilized *Rhizopus arrhizus*. (b) Application of Langmuir model for Mg(II) biosorption on the dead and immobilized *Rhizopus arrhizus*. (c) Application of Freundlich model for Mg(II) biosorption on the dead and immobilized *Rhizopus arrhizus*.

slope and intercept of a graph between C_e/q_e vs. C_e as shown in Fig. 3(b).

The values of $q_{\max}$ and b were 10.19 mg/g and 0.05, respectively. The Langmuir model demonstrated an adequate fitting to the data, using R^2; the coefficient of correlation was 0.929. This suggested that the elimination of Mg(II) by D.I.R.a. is in the shape of a single layer. As the value of R^2 was not unity, there was a compulsion to peruse a better depiction for the operation.

On the other hand, the Freundlich model is based on the binding sites heterogeneity and can be presented in the following correlation form [25]:

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

K_f and n are the Freundlich constants and they can be computed from the slope and intercept of a graph between $\log q_e$ and $\log C_e$ as shown in Fig. 3(c). The values of K_f and n were 0.74 and 1.62, respectively. The value of the correlation coefficient was 0.987, which gave us reason to believe that the Freundlich model was more appropriate in explaining the Mg(II) biosorption onto D.I.R.a. than the Langmuir model, hence preferred more. This is in reconciliation with the evidence of the presence of several binding sites (carbonyl, amines, phosphate group, etc.) [9].

3.4. Effect of temperature

Fig. 4 shows the dependency on temperature of the biosorption of Mg(II) onto D.I.R.a. A direct relation is observed between uptake and temperature. Following might be the possible number of reasons that are affiliated with the increase in uptake: (1) extension in number of active sites due to bond breakage at high temperature, (2) increase in kinetic energy of the metal ion resulting in the case of approach of Mg(II) to binding sites of D.I.R.a., (3) less effort is required in achieving the activation energy which is utilized in the formation of stable complexes, and (4) expansion of the pores might help the intraparticle diffusion to take place at larger magnitude [21,26–28]. As the process of biosorption of Mg(II) onto D.I.R.a. is complex, as pointed out in a previous section, so a consolidation of aforementioned mechanisms may be there to enhance the uptake of Mg(II) onto D.I.R.a. Since the increase in uptake from 5°C to 40°C was just 1.25 mg/g, it may be assumed that biosorption of Mg(II) onto D.I.R.a. is mainly caused by an energy independent mechanism.

3.5. Effect of co-ions

Fig. 5 defines a kinetic comparison of magnesium concentration profiles for different binary systems with magnesium as single component. It shows that equilibrium time was unchanged by the type of metal ion present, under a time limit of 60 min. However, the ratio of C/C_0 was greater at steady state for Cu + Mg systems as compared with a single component (Mg only). Due to the presence of Cu(II) ions, responsible for the combative effect, the concentration of Mg(II) in equilibrium binary system is greater than the single system. This is also responsible for the lower rate of removal of Mg(II). It can be interpreted that Cu(II) is in competition with Mg(II), to capture the available sites resulting in a lower uptake of Mg(II). The presence of Cu(II) inhibits the mixing of Mg(II), as a result of which Mg(II) was eliminated at lower rate, giving higher concentrations (C/C_0) of Mg(II) at equilibrium.

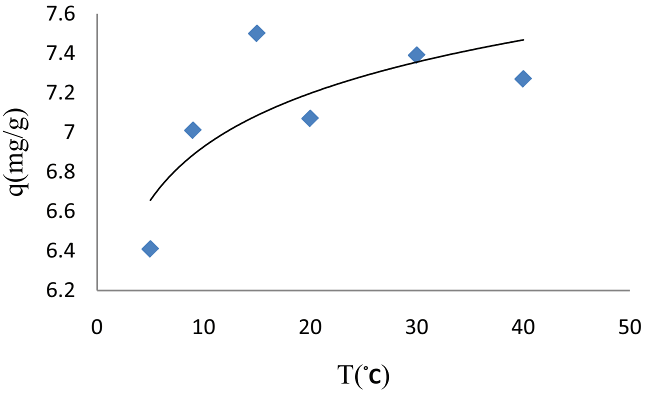

Fig. 4. Effect of solution temperature on the uptake of Mg(II) on the dead and immobilized *Rhizopus arrhizus*.

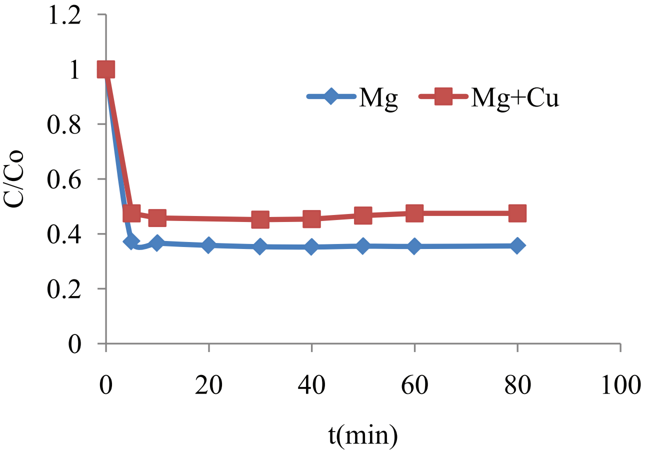

Fig. 5. Effect of co-ions on the uptake of Mg(II) on the dead and immobilized *Rhizopus arrhizus.*

4. Conclusion

In present study, D.I.R.a. is employed as a biosorbent for the removal of Mg(II) that seems to have promising prospects for the eradication of Mg(II) from aqueous solutions.

Following interpretations were made based on our research work:

- Maximum evacuation of Mg(II) by D.I.R.a. occurred at optimum pH value of 6.5, which was elected to further investigate other factors and parameters. It was also evaluated that overall pH of the solution or given sample decreased during biosorption of Mg(II) onto D.I.R.a.
- Equilibrium was gained within 60 min and a pseudo-second-order kinetic model appeared to be best fitting with an R^2 value of 1.000 and q_e value of 3.03 mg/g. The Weber and Morris model was adapted to figure

out the rate-determining step and it illustrated that the rate-controlling step is not the intraparticle diffusion and also, the biosorption of Mg(II) onto D.I.R.a. was due to chemisorption.

- The uptake of Mg(II) onto D.I.R.a. increased rapidly from 0.705 to 7.13 mg/g when initial dye concentration was raised from 2 to 100 mg/L. This indicates a promising percentage removal of Mg(II) by D.I.R.a.
- It was shown that both Langmuir and Freundlich isotherms possess good applicability with a high value of the correlation coefficient, however, it was found that the Freundlich model represented the Mg(II) biosorption onto D.I.R.a. more suitably as compared with the Langmuir model. The values of R^2, K_f, and n were 0.987, 0.74, and 1.62 respectively.
- The temperature showed impact on the Mg(II) uptake in the range of 5°C–40°C. The nature of the process of Mg(II) biosorption onto D.I.R.a. was found to be endothermic. It was seen that the effect of temperature on biosorption is less significant as compared with the effect of pH.
- Experiments with binary mixtures showed that equilibrium time was unchanged by the type of metal ion present within a time limit of 60 min, however, the presence of Cu(II) had an inhibiting effect on Mg(II) uptake by D.I.R.a.

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