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Zinc Biosorption by Waste Streptomyces fradiae Biomass: Equilibrium and Kinetics

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Abstract. Waste *Streptomyces fradiae* biomass from pharmaceutical industry was successfully used for Zn(II) removal from aqueous solutions. In the present study process parameters (initial pH of the solution, amount of biomass, initial metal concentration, stirring speed and contact time) and their influence on Zn(II) biosorption were investigated and optimized. Langmuir and Freundlich adsorption isotherms were used to describe sorption behavior between the waste biomass and the Zn ions. The biosorption process was better described by the Langmuir adsorption isotherm with 61.09 mg g^{-1} maximum adsorption capacity. Lagergren and Ho models were used to analyze the kinetic data. Ho model fitted better to the experimental results.

Key words: *Streptomyces fradiae*, biosorption, zinc, waste biomass, adsorption isotherms.

Introduction

Biosorption is an innovative technology for removal and separation of heavy metals from aqueous solutions. The search of low-cost sorbents for heavy metals is still an aim for the modern science. Microbial biomasses from industrial biotechnologies for production of different bioproducts, in particular antibiotics, are cheap and abundant byproduct that can be used as sorbent for heavy metal removal from wastewaters. By application of dead microbial mycelium for wastewater treatments two ecological problems can be solved. From one point of view the disposal of large amounts of waste biomasses is eliminated or decreased to a minimum. From another point of view a new and economically effective technology for purification of industrial waters contaminated with heavy metals is developed.

The biosorption is considered as an inexpensive and effective alternative to known technologies for heavy metal removal from wastewaters that offers some advantages, over traditional methods for metal removal, like low cost of the biosorbents, high-efficiency, no nutrient need, sludge minimization, regeneration of the biosorbents and the possibility for metal recovery (MACEK & MACKKOVA, 2011; ABBAS & SWADI, 2013). The biosrption is also a rapid process – in order of seconds or minutes (ATKINSON *et al.*, 1998).

Zinc is an essential microelement that takes part in different metalloenzymes, but

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in higher concentrations it can become toxic to humans and can give rise to serious poisoning cases. It is also on Environmental Protection Agency's list of priority pollutants (US EPA, 2009). The amount of Zn(II) in the drinking water should not exceed 3 mg dm^{-3} (WHO, 2008).

In the recent years many new biosorbents for Zn(II) removal were studied from agricultural wastes like rice husk (VIEIRA *et al.*, 2012) and sawdust (SHUKLA & PAI, 2005; MISHRA & TADEPALLI, 2014) to microorganisms like bacteria (MAMERI *et al.*, 1999; ÖZDEMIR *et al.*, 2009), algae (ZHOU *et al.*, 2011) fungi (DHANKHAR & HOODA, 2011) and yeast (HAMZA *et al.*, 2010).

Waste *Streptomyces fradiae* biomass obtained from tylosine production is a by-product that can be used as a low cost sorbent for Zn(II) removal from dilute aqueous solutions. *Streptomyces fradiae* is a gram-positive bacterium. The gram-positive bacteria are considered as sorbents with higher metal binding capacity than the gram-negative, owing to their different composition of the cell wall (GOURDON *et al.*, 1990; TARANGINI & SATPATH, 2009; NAJA & VOLESKY, 2011). The waste biomass may have some disadvantages, such as: the quality of the product might be variable and raw biomass may contain residual chemicals that could influence metal binding (NAJA & VOLESKY, 2011).

The aim of present study was to evaluate Zn(II) removal potential of caustic treated waste *Streptomyces fradiae* biomass. Influence of different parameters (pH, biomass amount, initial metal concentration, stirring speed and contact time) on the biosorption capacity was investigated. Langmuir and Freundlich adsorption isotherms were used to describe the biosorption equilibrium and pseudo-first and pseudo-second order equations were used to analyze the kinetic data.

Materials and Methods

Preparation of biosorbent and working solutions. For enhance biosorption performance the waste Streptomyces fradiae biomass was treated with 1M NaOH. The preparation of the biosorbent is described in our previous work (KIROVA et al., 2012). All working solutions were prepared daily from 1000 mg dm^{-3} Zn(II) stock solution prepared from $Zn(NO_3)_2.6H_2O$ (Merck). The desired pH of the working solutions was made with an appropriate amount of 0.1 M HNO_3 or 0.1 M NaOH.

Biosorption experiments

The biosorption was carried out in Erlenmeyer flasks containing 100 cm^3 of the metal solution with desired concentration, pH, amount of biosorbent, temperature, stirring speed. After the biosorption process, the biosorbent was separated from the solution by centrifugation. The remaining concentration of the metal ions in the solution was determined with PAR (5.10^{-3} mol dm^{-3}) as described by BARNARD & FKASHKA (1972). To calculate the metal uptake equation 1 was used.

$$q = \frac{(C_i - C_f)\,V}{W} \qquad (1)$$

where, C_i and C_f – initial and final metal concentration, mg dm^{-3}; V – volume of the solution, dm^3; W – amount of biosorbent, mg; q – metal uptake, mg g^{-1}.

The removal of the metal ions was found using equation 2.

$$R = \left[\frac{(C_o - C_f)}{C_o}\right].100,\% \qquad (2)$$

Influence of pH. The impact of the initial pH of the solution on the biosorption process was examined in the pH range from 2.0 to 6.0 at other optimal process conditions.

Influence of biomass concentration. The influence of the amount of biomass on the biosorption process was studied from 0.5 to 4 g dm^{-3} at pH 5.0, 50 mg dm^{-3} initial metal concentration, 300 rpm agitation speed and 120 min of contact time.

Influence of initial metal concentration. At pH 5.0, a biomass concentration of 1 g dm^{-3}, 300 rpm and 120 min of contact time the influence of the initial concentration on the metal uptake was examined. The concentration of the metal ion was varied from 10 to 200 mg dm^{-3}.

Influence of stirring speed. At optimal process conditions the effect of stirring speed on the biosorption process was studied. The stirring speed was varied from 50 to 350 rpm.

Influence of contact time. The influence of the contact time on the biosorption equilibrium and metal uptake was also examined. The initial concentrations of the Zn(II) were 25, 50 and 100 mg dm^{-3}. The amount of biomass was 1 g dm^{-3}, initial pH 5.0 of solutions and a stirring speed of 300 rpm. The experiments were carried out for different time intervals and the remaining concentrations of Zn(II) were determined.

Biosorption isotherms

For description of the biosorption process Langmuir and Freundlich adsorption isotherms were used. The biosorption of the Zn(II) ions was carried out in solutions with varying initial metal concentrations from 10 to 200 mg dm^{-3}. The experimental results were analyzed with the linearized forms of the Langmuir (equation 3) and Freundlich (equation 4) adsorption isotherms (VOLESKY, 2004):

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right) C_e + \left(\frac{1}{q_m b}\right) \qquad (3)$$

$$lg\, q_e = lg\, K_F + \left(\frac{1}{n}\right) lg C_e \qquad (4)$$

where: C_e – equilibrium metal concentration, mg dm^{-3}; q_e – equilibrium metal uptake, mg g^{-1}.

The maximum biosorption capacity q_m (mg g^{-1}) and Langmuir's constant b (dm^3 mg^{-1}) were determined from the linear plot of equation 3, obtained by plotting C_e /q_e versus C_e.

K_F – empiric constant linked to the maximum biosorption capacity (mg g^{-1} (mg dm^{-3})$^{-1/n}$), and n – constant related with the affinity between biosorbent and metal ions were determined from the linear relationship of lg q_e versus lg C_e from equation (4).

Kinetic modeling

The linear form of the Lagergren equation (WANG & CHEN, 2009) was presented as:

$$lg\,(q_e - q_t) = lg\, q_e - \left(\frac{k_1}{2{,}303}\right) t \qquad (5)$$

where, q_e and q_t – biosorption capacity at equilibrium and in the moment of time t (mg g^{-1}); k_1 – rate constant for pseudo-first order reactions (min^{-1}).

The linear form of the Ho equation (WANG & CHEN, 2009) was presented as:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \qquad (6)$$

where, k_2 is the pseudo-second order rate constant (g mg^{-1}min^{-1}).

From equations 5 and 6 the metal uptake at equilibrium and the kinetic constants of the process were found.

Results and Discussion

Influence of pH

The pH of the solutions plays a major role in the biosorption process. The charge of metal ions in the solution and the availability of active sites for heavy metals attraction onto the surface of biosobent depends mainly onto pH of the working solution. With the increasing of the pH from 2.0 to 6.0 the metal uptake and removal also increased (Fig. 1).

The low removal and uptake at pH 2.0 could be explained with the competition between the protons and the metal cations in solution for the adsorption sites on the biomass surface. The FTIR of the chemically treated biomass confirmed the presence of free hydroxyl and carboxyl groups on the surface of the biosorbent (KIROVA et al., 2012*).* When deprotonated carboxyl and hydroxyl groups are negatively charged and can bind positively charged zinc ions. With the increasing of the pH of the solution more functional groups on the cell wall are deprotonated and therefore provide more negatively charged groups for the Zn(II) biosorption (MAMERI *et al.*, 1999; KUJAN *et al.*, 2005; SAHMOUNE & LOUHAB, 2010). All further experiments were conducted at pH 5.

Influence of biomass concentration

The amount of the biosorbent also influenced the metal uptake and removal of the metal ions. With the increasing of the amount of the biosorbent, the number of the available sites for biosorption also increases, but the metal uptake per gram of biomass decrease (ESPOSITO *et al.,* 2001). With the increasing of the biomass dosage from 0.5 to 4.0 g dm^{-3} the metal uptake decreased from 50.32 to 6.79 mg g^{-1} (Fig. 2).

When the concentrations of the sorbent are too high it is impossible for metal ions to bind to all available active sites and that leads to low metal uptake (GADD *et al.,* 1988). The agglomeration of the biosorbent particles which decreased the contact surface and the active sites could explain the low metal uptake. Similar conclusions were made (SELATNIA *et al.* 2004a, 2004b) when other waste *Streptomyces* biomasses are used as biosorbents for metal ions.

Influence of initial metal concentration

To study the influence of the initial concentration on the biosorption performance the initial metal concentrations of the solutions were raised from 10 to 200 mg dm^{-3}. The obtained results are shown in Fig. 3.

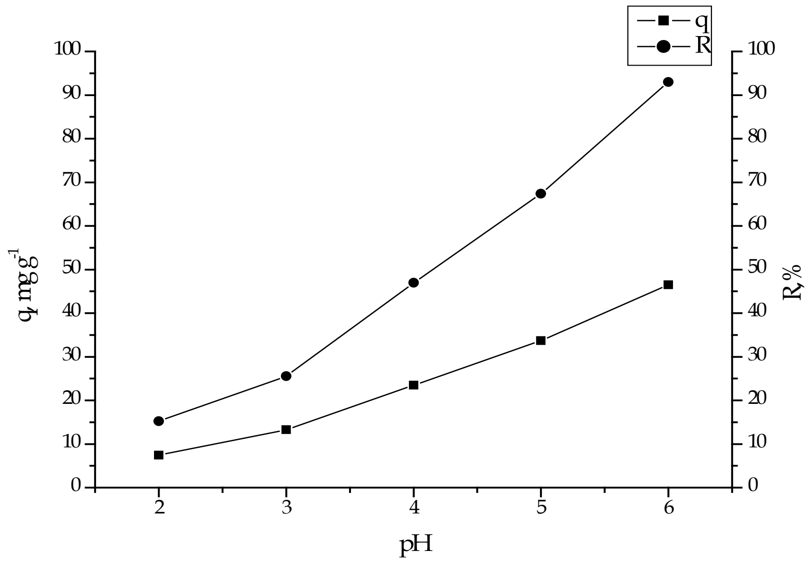

Fig. 1. Influence of pH on Zn(II) metal uptake and removal by waste *Streptomyces fradiae* biomass

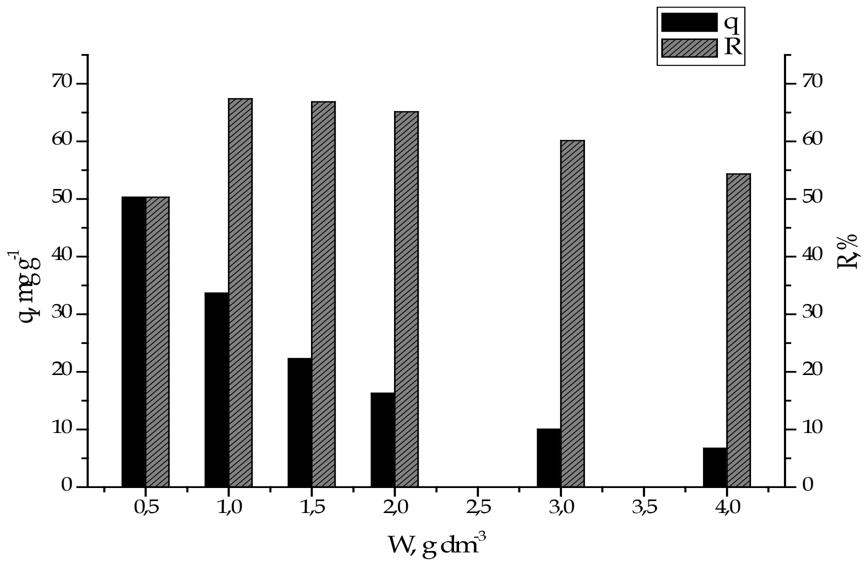

Fig. 2. Influence of the biomass concentration on Zn(II) uptake

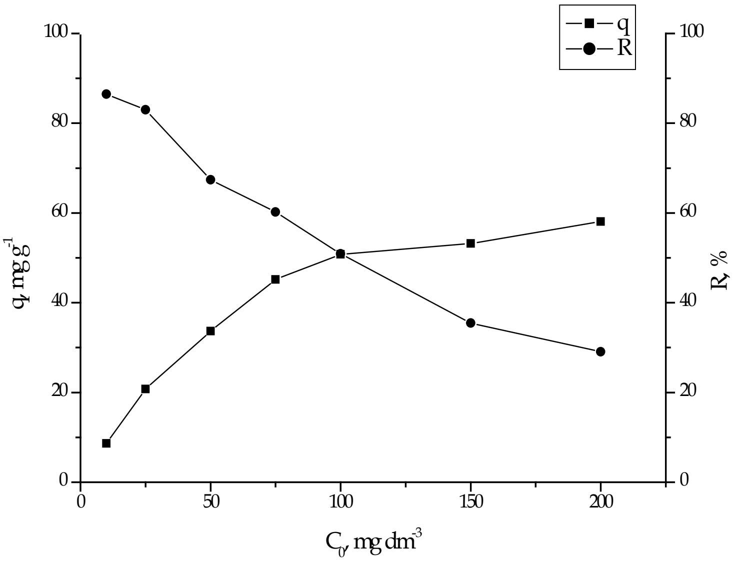

Fig. 3. Influence of the initial metal concentration on Zn(II) uptake and removal efficiency

With the increasing of the concentration of the metal ion from 10 to 75 mg dm^{-3} the metal uptake also increased from 8.65 to 45.15 mg g^{-1} and a plateau occurred. The removal of the metal ions varied from 86.5 to 29.05%. Different researchers have been examined the biosorption capacity of waste *Streptomyces rimosus* biomass chemically modified with NaOH for Zn(II) removal (MAMERI *et al.*, 1999), Pb(II) (SELATNIA *et al.*, 2004b), Cr(III) (SAHMOUNE & LOUHAB, 2010) with varying initial concentrations from 25 to 300 mg dm^{-3}. Due to different process parameters it is hard to compare the data but it is seen that with the increasing of the initial metal concentrations the metal uptake for gram biomass increase but the removal decrease.

Influence of stirring speed

The stirring speed also influenced the biosorption process (Fig. 4).

Agitation speed takes part in the contact between the metal ions and the biomass and influences the mass transfer in system sorbent-sorbat. Higher metal uptake of 33.69 mg g^{-1} and recovery of 67.38% were at 300 rpm. SELATNIA *et al.*, (2004b) explained the lower metal uptake at higher agitation speeds with the non-homogeneity of the sorbent-sorbat system as a result of vortex phenomena.

Influence of contact time

The time needed for equilibrium to be reached was analyzed with series of experiments. Fig. 5 shows that the biosorption of Zn(II) consists of two phases: a primary rapid one and a secondary slower phase. The Zn(II) uptake is rapid for the first 10 – 15 min of the biosorption process. When the initial concentrations were 25 mg dm^{-3} and 50 mg dm^{-3} equilibrium was reached for 40 min. After 60 min of contact time equilibrium was reached for all of the concentrations.

When the initial concentrations of metal ions are low there is abundance of free metal binding sites on the surface of the biosorbent and less metal ions in the solution to bind to them. The result is higher speed of the biosorption process. At higher metal concentrations the competition between metal ions for sorption sites decreased the biosorption speed. Similar results were reported by BAL *et al.* (2004). The biosorption of metal ions by *Streptomyces* species is a rapid process and equilibrium is reached from 20 to 180 min (MAMERI *et al.*, 1999; SELATNIA *et al.*, 2004b; KUJAN *et al.*, 2005; SAHMOUNE & LOUHAB, 2010).

Adsorpetion isotherms

For better understanding of the biosorption process and to describe the affinity between the metal ions and the waste biomass Langmuir and Freundlich adsorption models were used. The Langmuir adsorption isotherm suggests monolayer adsorption with fixed number of adsorption sites, in which the active sites on the surface on the biosorbent reacts with one molecule of the sorbat and once the active sites have been taken they don't react further. The Freundlich isotherm model describes biosorption on heterogeneous surface. The obtained constants and regression coefficients (Table 1), obtained from the linear plots of equations 3 and 4, had shown that the biosorption of Zn(II) by waste *Streptomyces fradiae* biomass was better described by the Langmuir adsorption isotherm.

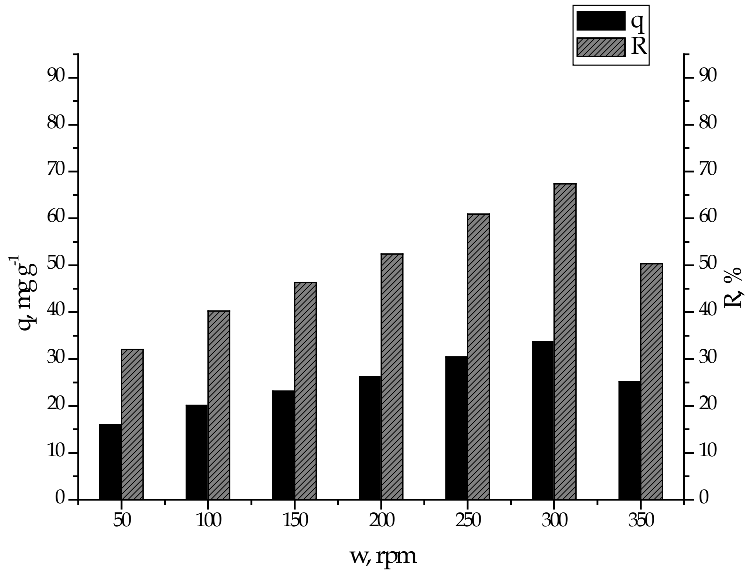

Fig. 4. Influence of stirring speed on Zn(II) uptake

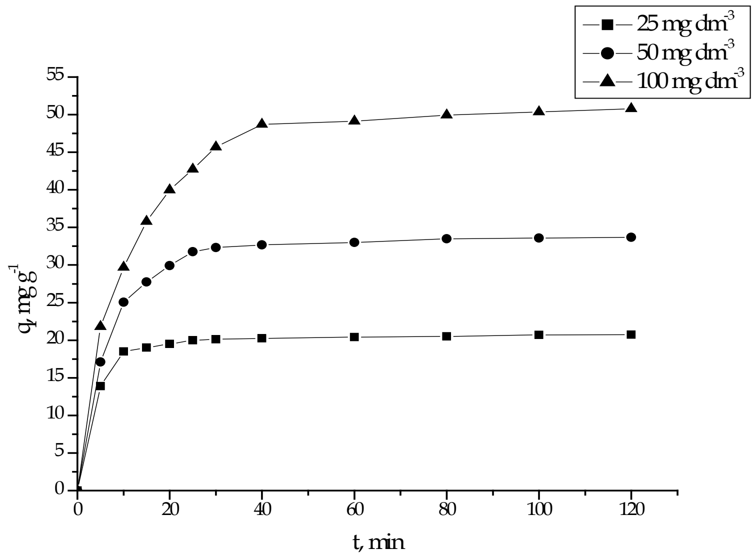

Fig. 5. Influence of contact time on Zn(II) biosorption

Table 1. Langmuir and Freundlich constants and correlation coefficients for Zn(II) biosorption by waste *Streptomyces fradiae* biomass

Langmuir model			Freundlich model		
q_{max}, mg g^{-1}	b, dm^3 mg^{-1}	R^2	K_F, mg g^{-1} (mg dm^{-3})$^{-1/n}$	n	R^2
61,09	0.097	0,999	9,91	2,56	0,965

Li *et al.* (2010) examined the biosorption capacity of living and dead *Streptomyces ciscaucasicus* CCNWHX 72-14 biomass for Zn(II) biosorption from aqueous solution and they also stated that the Langmuir model describes better the biosorpton process with maximum biosorption capacity of 42.75 mg g^{-1} for the living and 54 mg g^{-1} for the dead sorbents.

Kinetic modeling

The kinetic of the biosorption process was described by the pseudo-first order and pseudo-second order kinetic models of Lagergren and Ho. The Lagergren kinetic model (Fig. 8) is applicable for the first 20 – 30 min (rapid phase) of the biosorption process as the Ho model (Fig. 9) is suited for the whole range of contact time.

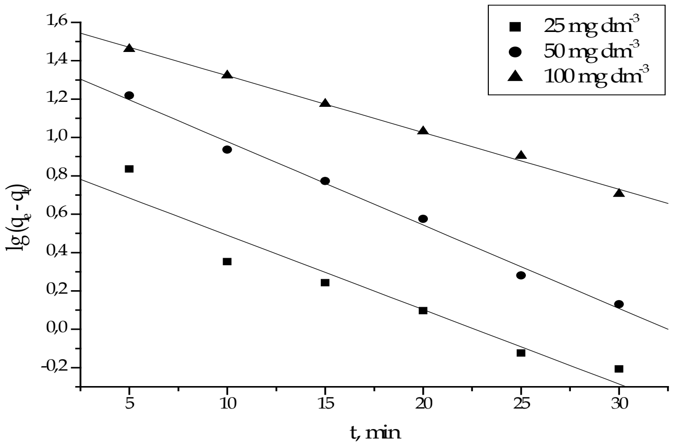

Fig. 8. Linear plot of Lagergren pseudo-first order kinetic model

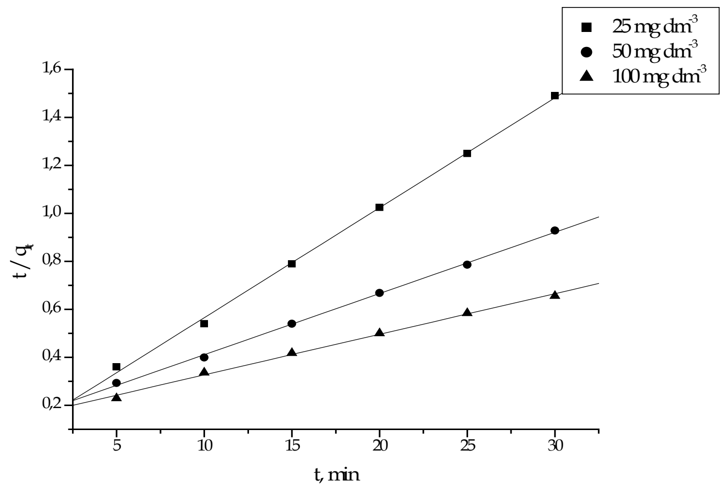

Fig. 9. Linear plot of Ho pseudo-second order kinetic model

Table 2. Pseudo-first and pseudo-second order kinetic parameters obtained for Zn(II) biosorption by waste *Streptomyces fradiae* biomass

Zn(II), mg dm^{-3}	$q_{(exp)}$, mg g^{-1}	Pseudo-first order			Pseudo-second order		
		k_1, min^{-1}	$q_{(model)}$, mg g^{-1}	R^2	k_2, g mg^{-1} min^{-1}	$q_{(model)}$, mg g^{-1}	R^2
25	20.75	8.93.10^{-2}	7.56	0.962	1,91.10^{-2}	21,97	0.999
50	33.68	1.01.10^{-1}	25.89	0.966	4,17.10^{-3}	39,20	0.999
100	50.77	6.82.10^{-2}	41.49	0.998	1,82.10^{-3}	59,98	0.998

The obtained constants, sorption capacities and correlation coefficients are shown in Table 2. As seen from the rable there is a good correlation between the experimental results and the kinetic data and the Ho kinetic model for pseudo-second order reaction fited better to the experimental results.

Conclusions

Based on the obtained results the following conclusions could be made:

Caustic treated waste *Streptomyces fradiae* biomass from tylosin production was found to be suitable and promising sorbent for Zn(II) removal from aqueous solutions with 61.09 mg g^{-1} maximum adsorption capacity, found by the Langmuir adsorption isotherm.

The kinetic data fitted well with the kinetic model for pseudo-second order reactions. The biosorption of the metal ion by the waste chemically treated sorbent is a rapid process.

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