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EQUILIBRIUM ISOTHERM STUDIES ON BATCH BIOSORPTION OF TOXIC NICKEL THROUGH FILAMENTOUS FUNGI

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Abstract

The release of metal-loaded wastewater is one of the most debatable environmental and health challenges faced by our community. Among different metals, nickel (Ni) is a commonly occurring potentially toxic element present in the environment due to various natural and industrial activities. Filamentous fungi are among the most economical biofriendly biosorbents, while adsorption through solid–liquid systems is well explained by the variety of isotherm models including Redlich-Peterson and Temkin isotherms. In the current study, all seven members of phylum Ascomycota including *Aspergillus niger*, *A. terreus*, *A. flavus*, *Rhizopus arrhizus*, *Alternaria alternata*, and *Trichoderma harzianum* showed considerable Ni removal efficiency over the concentration range of 25-100 ppm. The experimental accuracy of the equilibrium data relating to the influence of the initial metal concentration on the fungal biosorption capacity was more suitably explained by the three-dimension Redlich-Peterson isotherm due to the best fit of data (R^2 = 0.93-0.99) than the two-dimension Temkin isotherm (R^2 = 0.88-0.95). The results acquired represent the effectiveness of fungal species as a low-cost adsorbent for Ni(II) ions.

Keywords: Biosorption, heavy metal, isotherm, Nickel.

Introduction

The most important issue in Pakistan is the industrial wastewater contamination caused by the electroplating process. Due to the high concentration of heavy metals, the wastewater generated from these industrial units is relatively much less in volume but extremely poisonous in nature (Javaid *et al*., 2011; Shoaib *et al*., 2012). In general, heavy metals are harmful to humans even in very low amounts (Abd *et al*., 2015). For instance, the most prevalent toxins detected in industrial effluent are lead, mercury, copper, cadmium, nickel, and chromium (Bahadir *et al*., 2007). Among these, nickel (Ni) is the most prevalent element in the earth's crust and is a heavy metal with a silvery-white hue (Coman *et al*., 2013). Its natural concentrations in water range from 3 to 10 mg/L. (Prithviraj *et al*., 2014). For organisms living in an aquatic environment, nickel may even be hazardous at low doses (Ozer *et al*., 2008). When people are exposed to severely Ni-contaminated environmental media, a variety of pathological impacts on human health may manifest. Contact dermatitis, respiratory illnesses, cancers, cardiovascular problems, and kidney problems are some of these side effects. Nickel exposure can result from sources in the air, water, and food (Gurel, 2017).

Pollutants are removed from wastewater using a variety of biological, chemical, and physical (including adsorption) purification procedures (Rashid *et al*., 2021). The most common physicochemical procedure for assisting in the adsorption (a mass transfer process) of heavy metals involves an array of mechanisms, including adsorption, ion exchange, surface complexation, and the microprecipitation method for wastewater treatment (Javaid *et al*., 2011; Natrayan *et al*., 2022). The adsorption of heavy metal from the aqueous solution is made easier by the adsorbent's unique electrical and spatial characteristics.

Due to their abundance in nature, the presence of numerous functional groups (carboxyl, hydroxyl, amino, sulfonate, and phosphonate) for adsorption, the rigidity of the cell wall, the branching growth pattern, and a reasonable hypha diameter (2-10 m), filamentous fungi are among the most affordable biofriendly biosorbents that are available nowadays (Shoaib *et al*., 2012; Silva *et al*., 2019; Shah *et al*., 2020). In numerous earlier studies, the fungal biomass was employed to adsorb heavy metals from aqueous solutions, including Ni (Manzoor *et al*., 2012; Shoaib *et al*., 2013; Chen *et al*., 2019; Sharma *et al*., 2020). Literature also suggests many ways to employ isotherms to comprehend the adsorption process and adsorbent's capacity (Shoaib *et al*., 2013). The equilibrium relationships between the adsorbent and adsorbate are described by adsorption isotherms (Al-Ghouti, 2022). Several studies have employed the Langmuir, Freundlich, Temkin, BET, Redlich-Peterson, and Dubinin-Radushkevich isotherm models extensively for adsorption (Pulari *et al*., 2020). Therefore, it was considered that the Temkin and Redlich-Peterson isotherm would serve as a good design model for the biosorption system. The Temkin isotherm governs the influence of indirect adsorbate/adsorbate interactions on the adsorption process at an midrange ion concentrations (Shahbeig *et al*., 2013). Since the Redlich-Peterson (R-P) is the empirical isotherm, which combines components from the Langmuir and Freundlich equations. Hence, it is applicable for both homogeneous and heterogeneous systems to represent adsorption equilibrium at inclusive adsorbate concentrations (Gimbert *et al*., 2008). R-P isotherm approaches the Freundlich isotherm at high concentrations, approximating to Henry’s law at low concentrations (Aziz *et al*., 2020).

The current study was performed to evaluate the effect of the initial concentration of Ni ions on sorption performance of different fungal species along with the assessment of Temkin and Redlich-Peterson isotherms.

Materials and methods

Analytical grade nitrate salts of Ni metal ions (1000 ppm) were converted into stock solutions, by dissolving the exact amount of salt in double-distilled deionized water. The stock solution was further diluted into various concentration levels of 25, 50, and 75-100 ppm, respectively. The biomass of the fungal species (Table 1) was grown on 2% Malt extract broth (20 g Malt extract, 20 g agar in 1000 mL of the water). Followed by the incubation period of seven days, the biomass was filtered, dried in an oven (60 ℃) for 24 hours, and homogenized into 0.5-1 mm diameter fragments. Lastly, biosorbent (100 mg) was suspended in Ni solution (0.1 L) in a 250 mL flask, which was agitated at 150 rpm for three hours at pH 4.5 to conduct biosorption tests (Shoaib *et al*., 2012). For the statistical analysis, the experimental data were collected in triplicate to calculate mean values.

The data obtained from the adsorption experiments were analyzed through adsorption isotherms i.e. Temkin and Redlich-Peterson in order to investigate the adsorption mechanism (Table 2). The Temkin isotherm assumes the heat of sorption is linear, while Redlich-Peterson isotherm combines the Langmuir-Freundlich model and has three parameters to examine the biosorption data (Kumara *et al*., 2014).

Table 1: Fungal species obtained from the First Fungal Culture Bank of Pakistan (FCBP), Department of Plant Pathology, Faculty of Agricultural Sciences, University of the Punjab, Lahore, Pakistan

Fungi	Accession number
Aspergillus niger	FCBP 0074
Aspergillus terreus	FCBP 0058
Aspergillus flavus	FCBP 0064
Rhizopus arrhizus	FCBP 800
Alternaria alternata	FCBP 0092
Trichoderma harzianum	FCBP 0139
Cunninghamella echinulata	FCBP 0104

Table 2: Adsorption isotherm parameters

Temkin isotherm	$q_e = B_T lnA_T + B_T lnC_e$ B_T is the adsorption of heat constant, A_T is the binding equilibrium constant, and T is the absolute temperature
Redlich-Peterson isotherm	$In\ (K_R \frac{Ce}{qe} - 1) = b_R In\mathrm{Ce} + Ina_R$ K_R is the Redlich-Peterson adsorption capacity constant determined via trials and errors to obtain the maximum linear regression value of the isotherm graph. The parameter a_R is the R-P isotherm constant and b_R is the exponent between 0 and 1.

Results and Discussion

The current work investigated the usage of dried biomass of *R. arrhizus*, *T. harzianum*, *A. alternata*, *A. niger*, *A. terreus*, *A. flavus*, and *C. echinulata* for the adsorption of Ni from aqueous solution at varied concentrations (25, 50, 75 and 100 ppm) of Ni ions. Temkin and Redlich-Peterson isotherms were used to analyze the experimental data for Ni ion adsorption. The adsorption isotherm capacity not only determines the maximum adsorption capacity but also indicates how efficiently a biosorbent would adsorb and allows an estimate of the economic viability of the biosorbents for the specified solute (Shoaib *et al*., 2012).

Adsorption isotherms

It is impossible to determine the rate-determining step of the overall complex process of biosorption due to involvement of multiple factors including intra-particle diffusion, external mass transfer of solute, boundary layer diffusion, and adsorption at the active centers (Milenković *et al*., 2013). Nevertheless, sorption isotherm equations (e.g. Redlich–Peterson and Temkin isotherms) offer some quantitative evidence on functional equilibrium distribution through defining the sorption process, the surface properties and sorbent affinity with different concentrations of adsorbate in solution (Aziz *et al*., 2020). They offer advantageous in the assessment of adsorption capacity and to define the features of an adsorbent if suitable for application (Milenković *et al*., 2013).

Temkin Adsorption Isotherm

The Temkin isotherm was found to provide an appropriate representation of the data for Ni ions sorption onto the fungal biomass over the investigated concentration ranges (25-100 ppm,) of Ni ions (Inyinbor *et al*., 2016), as the value of R^2 was high (> 0.90), except for *C. echinulata* (Table 3; Fig. 1). According to the Temkin isotherm model, the adsorption heat of all molecules decreases linearly during the adsorption phenomenon due to surface coverage of adsorbant with adsorbate (Mir *et al*., 2018). The linear plots (q *vs* $\ln C_f$) and the values (9-16 kJ mol^{-1}) of Temkin isotherm constant (B_T) indicates a substantial interaction between the sorbate and the sorbent through chemisorption along with the uniform distribution of bounding energy up to some maximum bonding energy (Karthik *et al*., 2020).

Table 3: Temkin isotherm model parameters for biosorption of Ni (II) ions onto biomass of fungal species

Sr. No.	**Biosorbents**	A_T **(L/g)** Equilibrium constant	B_T **(J/mol)** Isotherm constant	R^2
1	*Rhizopus arrhizus*	136	16.61	0.95
2	*Trichoderma harzianum*	125	16.1	0.93
3	*Aspergillus niger*	114	15.71	0.92
4	*Aspergillus terreus*	114	14.38	0.91
5	*Aspergillus flavus*	113	12.60	0.95
6	*Alternaria alternata*	109	11.16	0.93
7	*Cunninghamella echinulata*	104	9.10	0.88

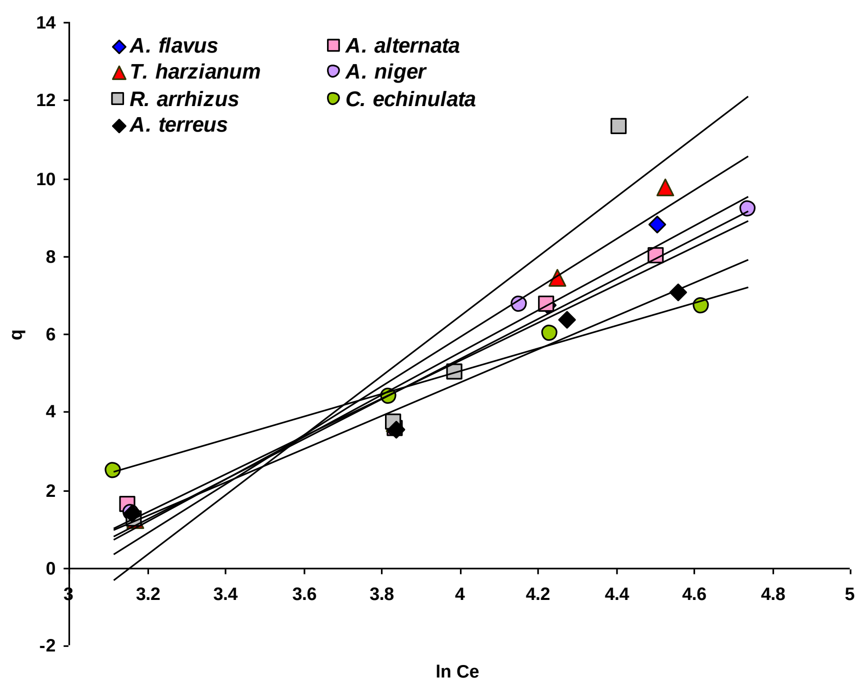

Fig. 1: The linearized Temkin adsorption isotherm for Ni (II) ions biosorption by fungal species. **Biosorption conditions:** Biomass quantity, 0.1g 100 mL^{-1}: pH, 4.5 at 150 rpm for 3 hrs.

Redlich-Peterson Adsorption Isotherm

The linear plot of R-P isotherm and parameters of the equation obtained for the sorption of Ni by different fungal species from the Ni solution are presented in Table 4 and Fig. 2. The R^2 values larger than 0.92 for all fungal species showed the proper fitness of experimental data in the Redlich-Peterson (R-P) equation. The value of b_R is usually between 0 and 1 (Wu *et al*., 2010), and the calculated values of b_R for the fungal species were within the prescribed range, demonstrating that adsorption data is accurately explained by this isotherm as well. The R-P isotherm model is unique, incorporates elements from both the Langmuir and Freundlich equations, and can be applied to both heterogeneous and homogeneous systems over a wide range of concentration (Redlich and Peterson, 1959). The accuracy of the three-dimension R-P equation has been evidenced in a number of studies as compared to two-dimension Langmuir, and Freundlich (Wu *et al*., 2010), hence R-P isotherm can be regarded as useful for characterizing the adsorption affinity to the biomass of fungi belonging to phylum Ascomycota. Moreover, b_R values for the *R. arrhizus*, *A. alternata* and *C. echinulata* for R-P isotherm parameters were greater than 1, which revealed that Langmuir model approximation better fits the experimental, while for the rest of fungal species, b_R values were less than 1 that might be due to fact that studied error functions of the isotherms were more closer to the Freundlich model (Aziz *et al*., 2020).

Table 4: Redlich-Peterson isotherm model parameters for biosorption of Ni (II) ions onto biomass of fungal species

Sr. No.	**Biosorbents**	a_R (ℓ·mmol^{-1}) Adsorption capacity	b_R Exponent	R^2
1	*Rhizopus arrhizus*	0.0089	1.31	0.93
2	*Trichoderma harzianum*	0.0022	0.88	0.98
3	*Aspergillus niger*	0.006	0.67	0.99
4	*Aspergillus terreus*	0.0087	0.56	0.99
5	*Aspergillus flavus*	0.0064	0.62	0.92
6	*Alternaria alternata*	0.0026	1.12	0.98
7	*Cunninghamella echinulata*	0.0010	1.09	0.99

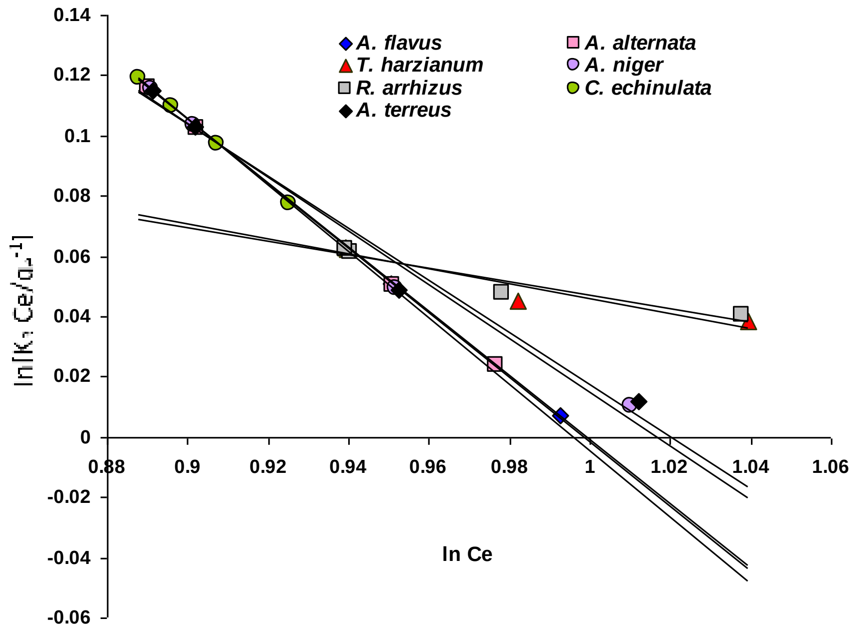

Fig. 2: The linearized Redlich-Peterson adsorption isotherm for Ni (II) ions biosorption by fungal species. Biosorption conditions: Biomass quantity, 0.1g 100 mL^{-1}: pH, 4.5 at 150 rpm for 3 hrs.

Conclusion

All seven fungal species viz., *A. niger*, *A. terreus, A. flavus, R. arrhizus, A. alternata,* and *T. harzianum* with the exception *C. echinulata* exhibited significant Ni removal efficiency. Experimental data obtained from batch equilibrium tests have been more appropriately explained by the three-dimension Redlich-Peterson isotherm model, which combines the features of Langmuir and Freundlich models than the two-dimension Temkin isotherm model.

Conflict of interest

Authors showed no conflict of interest.

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