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ORIGINAL PAPER

Study of Langmuir kinetics for removal of heavy metals by the fungal biomass

Aparna Gunjal[1]

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Abstract
The toxic heavy metals cause soil and water pollution. The heavy metals include cadmium, lead, zinc, arsenic, chromium, nickel, mercury, etc. There are physico-chemical methods for the removal of heavy metals from contaminated soils and water. The biosorption technique is easy, eco-friendly and economical for the removal of heavy metals from contaminated soils and water bodies. The work here describes the study of Langmuir kinetics for the removal of heavy metals by *Aspergillus clavatus*, *Aspergillus oryzae* and *Aspergillus fumigatus*. The fungi were isolated from the distillery spentwash-based composts and compost yard soil collected from the sugar factories viz., Theur, Malegaon and Baramati, Maharashtra, India. The Langmuir equations and constants were determined. The data showed the Langmuir isotherm model best fits the experimental data for biosorption of heavy metals viz., Zn, Pb and Ni and also second order pseudo kinetics is obeyed. The kinetics study will help to know curve of biosorption process. The study will be useful for the application of biosorption process on a large-scale.

Keywords Biosorption · Fungi · Kinetics · Physico-chemical · Atomic absorption spectrophotometer

Introduction

The heavy metals viz., zinc, cadmium, lead, nickel, mercury, arsenic, chromium, etc. are very toxic (Regine and Volesky 2000). The heavy metals cause soil and water pollution hazardous to the plants, animals and humans on the earth. The toxic heavy metals enter the food web due to leaching from contaminated soils and water. These heavy toxic metals pile up and increase in concentration called as "biomagnification" (Paknikar et al. 2003). The toxicity of the heavy metals originates with their ability to bind to the protein molecules, which stops replication of DNA and cell division (Kar et al. 1992). The biosorption technology can be used to remove heavy metals from the aqueous solutions. The biosorption technology is eco-friendly and economical, easy, and also helps in reuse of biomass with possibility of metal recovery. Another advantage is that these biological approaches are much safer as well.

The present work focuses on kinetics study i.e., Langmuir isotherm for the removal of heavy metals by the fungal biomass viz., *Aspergillus clavatus*, *Aspergillus oryzae* and *Aspergillus fumigatus*.

Material and methods

Fungi for sequestration of metals

The fungi used for the sequestration of metals were isolated by the viable count method from the distillery spentwash-based composts and compost yard soil. The distillery spentwash based composts and compost yard soil were obtained from the sugar factories viz., Theur, Malegaon and Baramati, Maharashtra, India.

Identification of fungi by slide culture technique

Half strength sterile Cdox agar medium [Cdox medium (g lit^{-1}): sucrose:4, $NaNO_3$:0.2, $MgSO_4.7H_2O$:0.05, K_2HPO_4:0.1, pH 7.0, agar:30] was prepared. Agar blocks (1cm^2) were cut and placed on sterile glass slide. The fungal

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✉ Aparna Gunjal
aparnavsi@yahoo.com

[1] Department of Microbiology, Savitribai Phule Pune University, Pune, India

isolates were inoculated to the four corners of the agar block. The slides were incubated at 28 °C for 3 days in the petri-plate on the glass triangle kept on the filter paper moistened with 20% glycerol. Staining was done by lactophenol cotton blue [lactophenol cotton blue (g l^{-1}): cotton blue:0.5, phenol:200, glycerol:400 mL, lactic acid:200 mL] and observed under phase contrast microscope.

Preparation of live biomass for sequestration of metals

The spore suspension (5×10^5 spores ml^{-1}) of the three fungi was used as inoculum for the preparation of biosorbents. The collected spores were aseptically transferred to 500 mL conical flask containing 100 mL Yeast Peptone Glucose (YPG) [YPG (g l^{-1}): yeast extract:3, peptone:10, glucose:30, pH:4.5] broth and incubated on a rotary shaker (125 rpm) at 28 °C for 3 days. The biomass was harvested and washed with deionized water, which was 'live biomass'. The biomass was used for further Langmuir kinetics study of biosorption of heavy metals viz., Zn, Pb and Ni.

Kinetics study

Batch adsorption tests were done at 38 °C. For each test, 0.5 g of the fungal biomass viz., *A. clavatus*, *A. oryzae* and *A. fumigatus* was mixed into 50 mL solution of metal concentration ranging from 5 to 25 ppm. The contact time maintained was 20 min. Each mixture was filtered and the metal content was determined by Atomic Absorption Spectrophotometer (AAS) (AAS-Varian SpectraA, Germany). The kinetics results are expressed in terms of Langmuir isotherms.

Results and discussion

Identification of the fungal isolates

The fungi isolated from the distillery spentwash-based composts and compost yard soil by slide culture technique was identified to be *Aspergillus clavatus*, *Aspergillus oryzae* and *Aspergillus fumigatus*.

Linear regression equations of langmuir isotherm for biosorption of heavy metals by the fungal biomass

The linear regression equations of Langmuir isotherm for biosorption of heavy metals by the fungal biomass viz., *A. clavatus*, *A. oryzae* and *A. fumigatus* is are shown in Table 1.

Langmuir isotherm constants for biosorption of heavy metals by the fungal biomass

The Langmuir isotherm constants for biosorption of heavy metals by the fungal biomass are shown in Tables 2, 3 and 4 respectively. The Langmuir isotherm (Langmuir 1918) is calculated from the equation

$$C_e/\,Q_{0=}1/\,q_{max}R_L + \left(C_e/\,q_{max}\right) \quad (1)$$

where, C_e = equilibrium concentration (mg l^{-1}), Q_0 = amount adsorbed at equilibrium (mg g^{-1}), q_{max} = Langmuir constants related to biosorption capacity and R_L = energy of adsorption.

There is a report on Langmuir adsorption study for removal of platinum and palladium from waste water by

Table 1 Linear regression equations of Langmuir isotherm for biosorption of heavy metals by the fungal biomass

Fungal biomass	Heavy metals		
	Zn	Pb	Ni
A. clavatus	y = -3.181x + 26.45	y = 7.578x + 132.17	y = -0.417x + 24.58
A. oryzae	y = 0.619x + 11.25	y = -14.45x + 212.2	y = -0.944x + 26.65
A. fumigatus	y = -3.181x + 26.45	y = 214.49x—215.49	y = -2.299x + 29.47

Table 2 Langmuir isotherm constants for biosorption of heavy metals by *A. clavatus*

Metals	Heavy metal conc. (ppm)				
	5	10	15	20	25
	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})
Zn	0.20	0.46	0.94	1.44	1.92
Pb	0.04	0.08	0.14	0.22	0.24
Ni	0.20	0.40	0.58	0.96	1.00

Table 3 Langmuir isotherm constants for biosorption of heavy metals by *A. oryzae*

Metals	Heavy metal conc. (ppm)				
	5	10	15	20	25
	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})
Zn	0.20	0.46	0.94	1.44	1.92
Pb	0.02	0.08	0.10	0.11	0.16
Ni	0.18	0.38	0.62	1.04	0.94

Table 4 Langmuir isotherm constants for biosorption of heavy metals by *A. fumigatus*

Metals	Heavy metal conc. (ppm)				
	5	10	15	20	25
	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})	q_{max} (mg g^{-1})
Zn	0.20	0.46	0.94	1.44	1.92
Pb	0.04	0.04	0.04	0.13	0.02
Ni	0.18	0.38	0.62	0.98	1.30

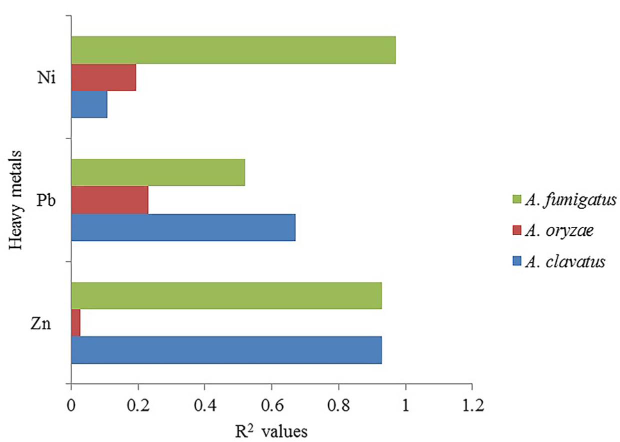

Fig. 1 R values for Langmuir isotherms

means of biosorption on fungi *Aspergillus* sp. and yeast *Saccharomyces* sp. (Godlewska-Zylkiewicz et al. 2019). Also, kinetics study is done on biosorption of lead and copper using mushroom biomass *Lepiota hystrix* (Kariuki et al. 2017). Bishnoi et al. (2007) have studied kinetics for biosorption of Cr (VI) with *Trichoderma viride* immobilized fungal biomass and cell free Ca-alginate beads. There are few reports on the kinetics study of biosoprtion of Zn, Pb and Ni by *A. clavatus*, *A. oryzae* and *A. fumigatus*.

R^2 values for langmuir isotherms

The R^2 values for Langmuir isotherms are shown in Fig. 1. The R^2 values are < 1.

Conclusion

The biosorption kinetics study showed that Langmuir isotherm models best fit the experimental data for the biosorption of heavy metals viz., Zn, Pb and Ni. The Langmuir kinetics data are best modeled by a pseudo-second-order kinetics equation.

Declarations

Conflict of interest The author declares no conflict of interest.

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