

BIOSORPTION OF MERCURY FROM WASTEWATER USING ISOLATED ASPERGILLUS Sp. MODIFIED 1,10-PHENANTHROLINE: HILL ISOTHERM MODEL

Shameran J. Salih ^{a,*}, Sewgil S. Anwer ^b, Rezhna H. Faraj ^a

^a Dept. of Chemistry, Faculty of Science and Health, Koya University, Koya, Kurdistan Region, Iraq – (shameran.jamal, rezhna.hassan)@koyauniversity.org

^b Dept. of Clinical Biochemistry, College of Health Science, Hawler Medical University, Erbil, Kurdistan Region, Iraq – (dr.sewgil75@gmail.com)

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ABSTRACT:

Equilibrium biosorption of mercury (II) onto new developed biosorbent (1,10-phenanthroline-graft- cell/Filamentous fungi) in both free, immobilized and dead cell were investigated. The product was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). In this work several isotherm models applied to predict the process design for the adsorption system. Hill, Sips, Langmuir and Freundlich utilized to determine the adsorption parameters, the equilibrium data fitted well to Hill and Sips isotherm models followed by Langmuir. Meanwhile, the maximum adsorption capacity proposed by Hill model was 78.67(mg/g) and Sips 78.42(mg/g) were lower than Langmuir models which was 85.16(mg/g). In other hand, the equilibrium data almost fitted to the Freundlich isotherm supporting the postulation of the heterogeneous shape of biosorption to certain range. Hence, On the bases of Langmuir model the biosorption of Hg²⁺ onto 1,10-phenanthroline-graft- cell/Filamentous was in the favourable area and that confirmed by calculating the separation factor (RL < 1). Nevertheless, new isotherm (Eq. 4) has been derived by the combination of a Langmuir and Freundlich models. The new model agreed well enough (R² = 0.9863) with the experimental data.

KEYWORDS: Hill and Sips isotherm, Biosorption, Modified-Aspergillus Sp. Wastewater.

1. INTRODUCTION

Heavy metal ions are non-degradable and highly toxic even at low concentration. Environmental mercury levels have increased considerably in recent years. The direct anthropogenic sources of mercury in water bodies are related to numerous industrial applications (e.g., chloroalkali productions, pharmaceutical and cosmetic preparations, electrical instruments, and pulp and paper industries) and many products of common use (e.g., thermometers, batteries, and medical drugs) (Pavlish et al., 2004). Hg (II) is the poisonous metal ions that cause both acute and chronic toxicity to the central nervous system, kidneys, lung tissues, and reproductive system (Adams et al. 2005). Removal of heavy metal using living or dead organisms has received more attention in recent years because of their potential application in environmental protection.

The expression of biosorption is utilized to characterize the passive non- metabolically mediated process of heavy metal linkage to living or dead biomass (Rangsayator et al., 2002). Biosorption of Hg (II) from aqueous solutions can be examining as an alternative technology in treatment of industrial wastewater. The technique is emerging technologies depend on the power of biological materials to uptake heavy metals from wastewater by either physico-chemical or metabolically mediated pathways of removal process (Brinza et al., 2007).

A set of inexpensive biomass has been investigated and manufactured for removal of pollutant from aquatic system in various parts worldwide (Kar & Misra, 2004). They include algae (Elifantz & Tel-Or, 2002), fungi (Conesa et al., 2005), anaerobically digested sludge (Tokcaer & Yetis, 2006) and bacteria (Liu et al., 2006). Waste materials have also been.

These include groundnut husk (Okieimen et al., 1985), rice bran, soybean and cottonseed hulls (Marshall et al, 1999), coir, jute and sawdust (Shukla & Pai, 2005), crop milling waste (Aubert et al., 2005), canola meal and coconut shell (Ajayi et al., 2002) amongst others. Generally, microorganisms are used closely in diverse food-pharmaceutical industries, they are created as waste, which can be achieved free or at low-cost from these industries. Nevertheless, they show high capabilities in adsorption of organic and inorganic toxicity from aqueous solutions. This is due to the presence of alginates, which is present in gel form in their cell walls. Also, their macroscopic structure proposed a proper basis for the produce of bio sorbent particles that are convenient for adsorption process applications. Lately, many approaches have been made for the evaluation of low cost adsorbents from agriculture wastes and industries.

Meanwhile, it is principally the cell wall of certain bacteria, fungi and algae which is found to be responsible for the process of biosorption. The cell wall of cyanobacteria involves hydroxyl, carbonyl, carboxyl, sulphahydryl, sulphonate, amine, imine, imidazole, phosphor diester groups and thioether (Venkatesh et al., 2003).

Here, Filamentous fungi (Aspergillus, Penicillium, Rhizopus and Mucor) may be utilized in biosorption process (Gaad, 1990). The cell wall of the fungi is the first to come into contact with metal ions in solution, due to high electron exchange capacity of their cell walls. These features arise from large density of functional groups in the cell wall that create a negative charged surface (Ledin et al, 1996).

Finally, the objective of this study is to design a new composite biosorbent by introducing 1,10-phenanthroline into a cell/Filamentous fungi, as an alternative modified adsorbent for the removal of Hg(II) ions from aqueous solutions. In this work, different parameters have been investigated such as effect of

* Corresponding author

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initial Hg (II) solution, contact time, concentration on adsorption, pH and temperature was evaluated and compared with 1,10-phenanthroline-graft- cell/Filamentous fungi-binding Hg.

2. MATERIALS AND METHODS

2.1 Materials

All reagents were for analytical grade and used without further purification, Mercury Chloride (Sigma -Aldrich), 1,10-phenanthroline (Analar), hydrochloric acid 37% (Merck), sodium hydroxide(Sigma-Aldrich), potassium chloride (Aldrich), potassium hydrogen phthalate (Merck),sodium hydrogen carbonate (Sigma -Aldrich) and potassium hydrogen phosphate (Merck) were used to prepare the buffer solutions with different pH values.

2.2 Instruments

Instruments that have been used in this work are listed in the Table 1.

Instruments	Made	Function
Spectrophotometer (UV/Vis)	Aglient Technology Cary UV-Vis spectrophotometer	Absorbance
Scanning Electron Microscopy (SEM)	NORAN	Images providing compositional, morphological and topographical information
Sensitive weight balance	HTCE 3000g 0.01g	To measure weight
Incubator shaker	GFL 3031	To shake the samples
Oven	Desert Chamber Pro	To dry samples
PH meter	pH/Ion 510	Measurement of pH
FT-IR	SHIMADZU	To obtain spectrum of absorption

2.3 Preparation of Biosorbent

Sample Collection and Fungus Isolation: Soil samples were collected from area near to waste products. The soil samples were transported to the laboratory for fungal isolation. Different dilutions such as 10⁻³ -10⁻⁶ were prepared from this stock solution in sterile distilled water under aseptic conditions. 0.1 ml of diluted suspension placed on PDA plates contain 25mg Chloramphenicol to inhibit bacterial growth. Plates were incubated at 25°C for 5-7 days. After sub culturing on PDA pure culture obtained and fungal colonies were identified according to morphological and microscopic characteristics (Nagamani et al., 2006).

2.4 Composite Matrix

First, 8% (w/v) of fungal colonies were mixed with fresh 10% (w/v) of 1,10-siphenanthroline then agitated overnight in a controlled temperature (30°C) and shaking 180rpm in an incubator shaker. The sample was filtrate washed by deionized water/3 times then oven-dried at 50 °C for 10 hrs. Finally, the obtained biomass (1,10-phenanthroline-graft-cell/Filamentous fungi) kept in a dissector for moisture avoided. In addition, all instruments that used for this work are summarized in Table 1.

2.5 Batch Equilibrium Studies

The adsorption of Mercury and removal efficiency by the composite matrix was investigated using the batch equilibrium method. A solution of 40 mg.L⁻¹ of Hg²⁺was prepared by dissolving 0.0541g of mercury chloride in1000ml of deionized water then a 50 ml of Hg²⁺ solution was prepared and equilibrated using a magnetic stirrer. Different amount of biosorbent have been tested (20, 40, 60, 80 and 100 mg) was then suspended in the Hg²⁺solution and shaken until equilibrium time is reached. After filtration, the amount of adsorbed Hg²⁺ ions was calculated from the variation between the initial and final concentration (Non-adsorbed molecules) of Hg²⁺ions,measured by UV-visible spectrophotometer at a wavelength of 575 nm. (Rashid et al., 2016). Furthermore, in order to study the effect of temperature on the adsorption process the batch performed at different temperatures, also various solution pH have been conducted (pH= 3, 7, and 10). The removal of mercury per unit mass of biosorbent was then calculated through mass-balance calculations (Gladstone, et al., 2015):

$$q_e = \frac{C_o - C_e}{W} \times V \quad (1)$$

where q_e = Amount of adsorbed Hg²⁺ (mg/g)
 C_o = Initial concentration (mg.l⁻¹)
 C_e = Equilibrium concentration (mg.l⁻¹)
 W = Mass of adsorbent (mg)
 V = Solution volume (ml)

The removal percentage was determined using the equation below (Salih, 2014):

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where C_o and C_e = Initial and final Hg²⁺ concentration (mg.l⁻¹)
 $R\%$ = Removal percentage

Also, scanning electron microscopy (SEM) was used to identify the surface morphology of the prepared adsorbent (model HTCE 3000g 0.01g) which was dried for 24 hrs at 105 °C before SEM loaded.

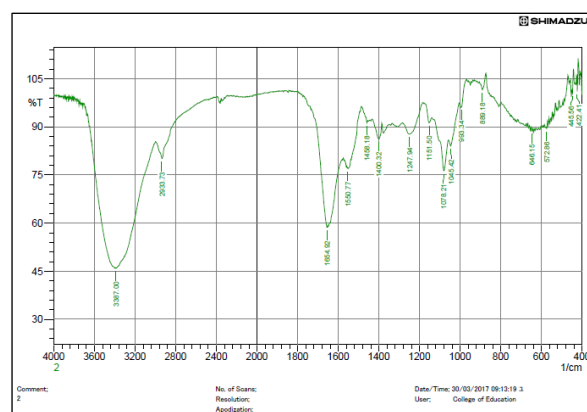


Figure 1. FT-IR analysis of biosorbent loaded 1,10-phenanthroline-graft- cell/Filamentous fungi.

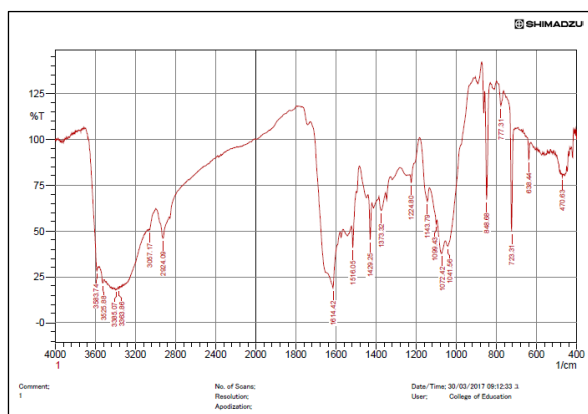


Figure 2. FT-IR analysis of biosorbent loaded 1,10-phenanthroline-graft-cell/Filamentous fungi-binding Hg.

3. RESULTS AND DISCUSSTION

3.1 FT-IR Characterization

The important Infrared spectra of the complex (1,10-phenanthroline-graft-cell/Filamentous fungi-binding Hg) is compared with the Infrared of the ligand (1,10-phenanthroline-graft-cell/Filamentous fungi) for determining the changes happened, significant picks from Figure 1 and Figure 2 are listed in the Table 2. The absorption stretching band of C=O, and C=N aromatic ring appeared at 1654 cm⁻¹ and 1550 cm⁻¹ in the ligand is shifted toward slower wave number in the complex that appear at 1614 cm⁻¹ and 1516 cm⁻¹ respectively, which indicates coordination via C=O of the fungi and the nitrogen atoms from the 1,10-phenanthroline. This is also confirmed by the appearance of a new band at 470 cm⁻¹ in the complex which assigned to the Hg-N bond (Ranjbar et al., 2013).

Table 2. Selected IR Spectral of ligand and complex (cm⁻¹)

	O-H	C=N	C=O	(C-H) group	Hg-N
Ligand (1,10phenanthroline)	3387	1550	1654	2933	---
(Hg_ Ligand) complex	3385	1516	1614	2924 3057	470

3.2 Microscopically Study

Microscopically examination from soil isolates showed that Conidiophores and septate, unbranched hyphae, with a swollen apex (vesicle), conidia in dry chains forming compact columns (columnar) that can be identified as *Aspergillus* Sp. As shown in Figure 3. The same study observed by (Gladstone, et al., 2015).

3.3 Scanning Electron Microscopy (SEM) Analysis

The morphology of the biosorbent, 1,10-phenanthroline and composite matrix which is 1,10-phenanthroline-graft-cell/Filamentous fungi-binding-Hg have been examined using SEM with magnification of 10 000 to indicate the porous sites of cell/Filamentous fungi as shown in Figure 4-A, further Figure 4-B and 4-C elucidate the successful loaded of 1,10-phenanthroline and binding with Hg²⁺ respectively. Meanwhile, the composite matrix demonstrated some micro-cracks in the surface (Zhang et al., 2012). Nevertheless, the particles are mostly irregular in shape and circular within

indication of a rougher surface in the composites with a higher content of 1,10-phenanthroline, this characteristic change in the analyzed SEM images emphasize the presence of 1,10-phenanthroline and mercury in the surface of cell/Filamentous fungi.

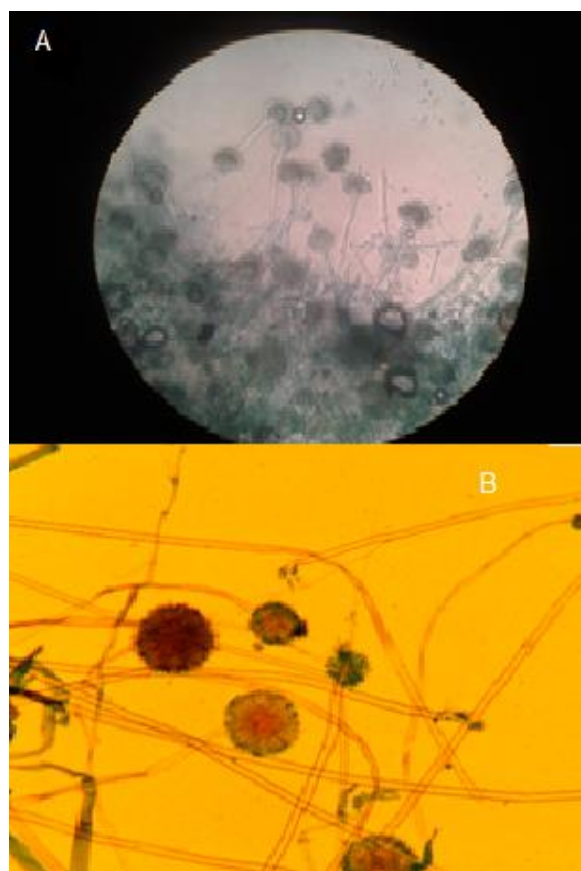


Figure 3. A. *Aspergillus* sp. under microscope, B. *Aspergillus* sp. Under microscope stained with lactophenol

3.4 Biosorption Mechanisms

The microorganism associates with heavy metals by a composite of different metal binding mechanisms involved physisorption, ion-exchange and complexation (Venkatesh et al., 2003). Nevertheless, the physisorption as explained from previous studies (Ahalya et al., 2003) which includes the electrostatic interaction (Van der-waals forces) occur between the cell wall of microbes and metal ion in the solution. However, these interactions are responsible in mercury biosorption utilize *Aspergillus* Sp. Furthermore, the biosorptive process as described by complexation mechanisms occurs onto biosorbent via formation of coordinate bonds between the reactive groups on the surface of cell wall and the metal ion. Moreover, Similar results are confirmed elsewhere (Gladstone et al., 2015). Here, attempts were made to evaluate different type of the *Aspergillus* Sp. involves free cell, immobilized and dead cell in removal process, as the Figure 5 indicate that the dead cell of the biosorbent showed high ability for mercury uptake in adsorptive study.

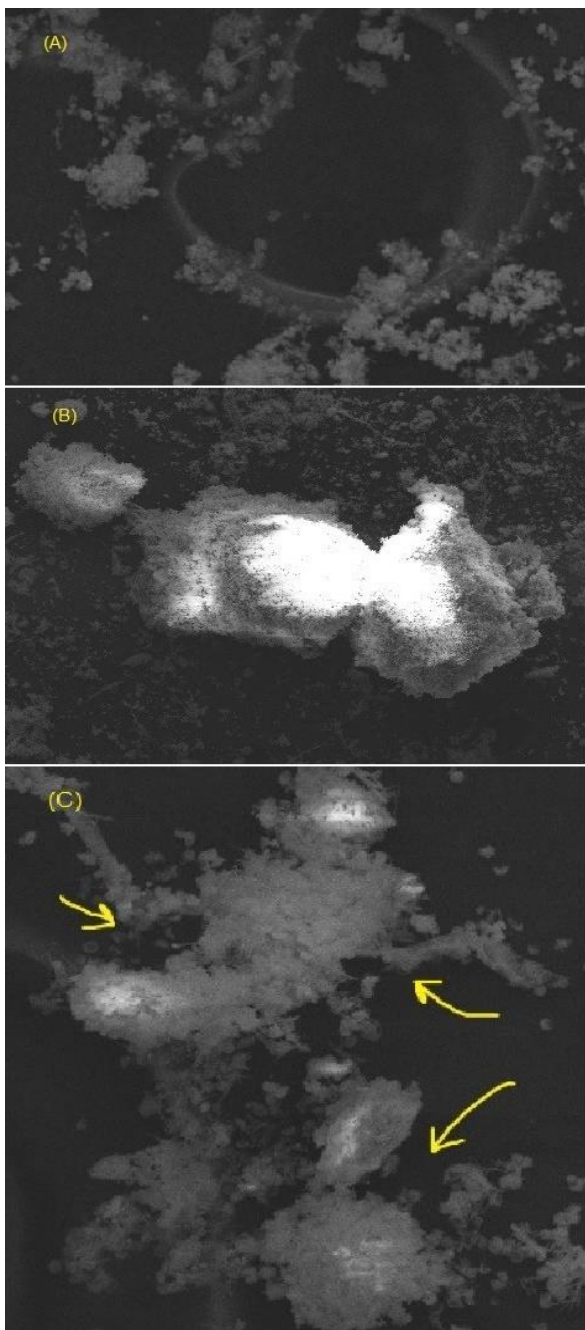


Figure 4. (A, B and C): SEM images cell/Filamentous fungi, 1,10-phenanthroline loaded and modified biosorbent binding Hg²⁺ respectively

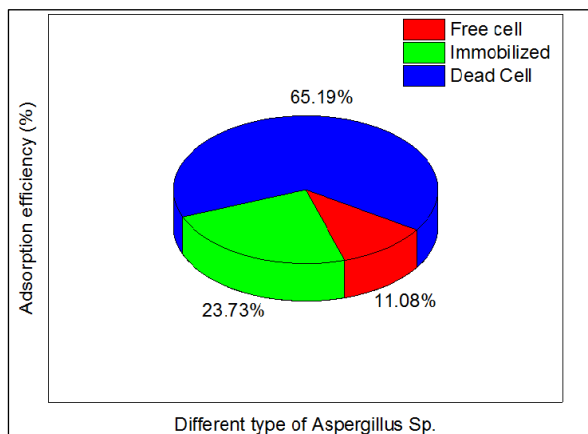


Figure 5. Different type of Aspergillus Sp. Loaded in removal process

3.5 Study of parameters that have effect on the adsorption process

3.5.1 Effect of Initial Biosorbent Dosage: The effect of biosorbent on the adsorption of Hg²⁺ are showed in Figure 6, it is easily understood that the biosorption efficiency increased with increasing the amount of biosorbent until reached maximum uptake of 89% Hg²⁺ at a certain limit 500mg of the biosorbent. At the first stage, rapid increase of biosorption of mercury (II) with the increase in the amount of 1,10-phenanthroline-graft-cell/Filamentous fungi perhaps attributed to high availability of binding sites (Salih, 2014). However, all the available sites have been covered by the metal-complex, but after this critical dosage (500mg) of the biosorbent the number of binding sites increases with slower of biosorption rate, since all the active sites may not obtainable due to overlapping between sorbent sites themselves and/or shortage of the concentration of Hg²⁺ in the solution (Nowicki et al., 2013).

3.5.2 Effect of pH on biosorption of mercury onto AspergillusSp: In a biosorption process it is quite important to evaluate the effect of pH in order to maintain the amount of adsorption capacity. Biological evolution also based on the pH of the aqueous media (Zhang et al., 2012). In this work, three different pH solution have been examined (pH 10 = 3, 7 and 10), this procedure perhaps elucidate by the study of pH point zero charge (pHpzc) which describe the net surface charge of the biosorbent when equal to zero. In other word, drift method used to determine the pH point zero charge (pHpzc = 6). Figure 7(A and B) demonstrate that higher adsorption capacity (mg/g) and higher adsorption efficiency (%R) occurred at pH=3 in comparison to pH= 7 and 10. This may due to, that the solid surface adsorbed positive charge from the acidic solution while the pH equal 3 the predominate form in the solution are HgCl₂ and HgCl₃⁻ (Patil & Shrivastava, 2010) followed by electrostatic interactions between the solid surface and the negative forms of complexes metal intend to increase the biosorptive process. As confirmed by figure 7(A and B) when the pH of the solution increased (pH =7) the adsorption capacity and adsorption efficiency decreased because there is not a significant interactions between adsorbate and the adsorbent. In this case the net charge is closed to pHpzc (net surface charge = zero). Finally, when the solution achieved at pH equal 10 the biosorption rapidly diminished for the reason that electrostatic repulsion are dominant between negative charged of the solid surface and the metal ion and this biosorption more difficult. Similar studies reported elsewhere (Chakraborty et al., 2011).

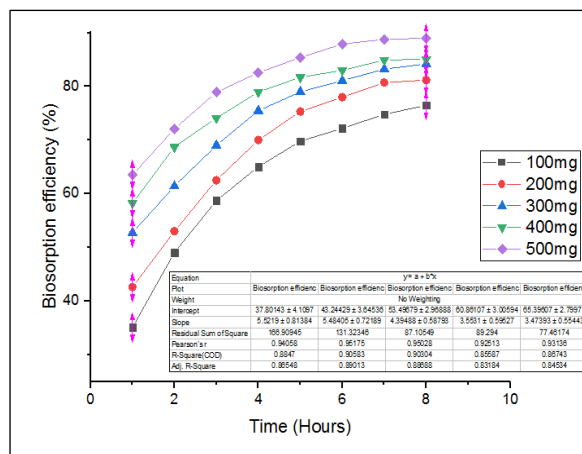


Figure 6. Effect of biosorbent dose on removal of Hg²⁺ onto Aspergillus Sp. initial Hg²⁺ concentration 50mg/L, temp 298K, shaking speed 180rpm.

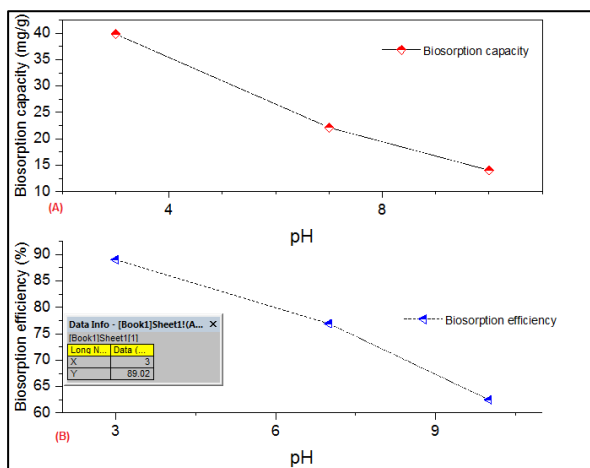


Figure 7. A- biosorption capacity of mercury onto *Aspergillus Sp.* in different pH solution, B- biosorption efficiency of mercury onto *Aspergillus Sp.* in different solution pH

3.5.3 Effect of temperature on biosorption of mercury onto *Aspergillus Sp.*: The biosorption of mercury onto *Aspergillus Sp.* was studied at different temperatures of 25, 35, 45 and 60 °C. In the spite of the fact that heat plays a major role in biosorption process based on the stability of cross-linked of microorganism-metal complex (Salih & Rashid, 2015). Figure 8 showed that the biosorption efficiency inversely change with increasing temperature as confirmed from obtained data. However, the metal uptake decreased from 71.44% to 47.92% at 298K to 333K respectively. This refers to the weakening interaction of sorbent sites and the metal ion which was explained by Vander Waals interaction that occurred between the modified *Aspergillus Sp.* and Hg^{2+} . Meanwhile, the loading capacity decrease with rise of temperature. In other word, the rate of desorption is more noticeable than the rate of biosorption and it is quit evidence that the biosorption of mercury onto 1,10-phenanthroline-graft- cell/Filamentous fungi is an exothermic process (Nowicki et al., 2013). Finally, the obtained results propose that a high temperature is not preferable for biosorption of 18 Hg^{2+} when the 1,10-phenanthroline-graft- cell/Filamentous fungi is biosorbent.

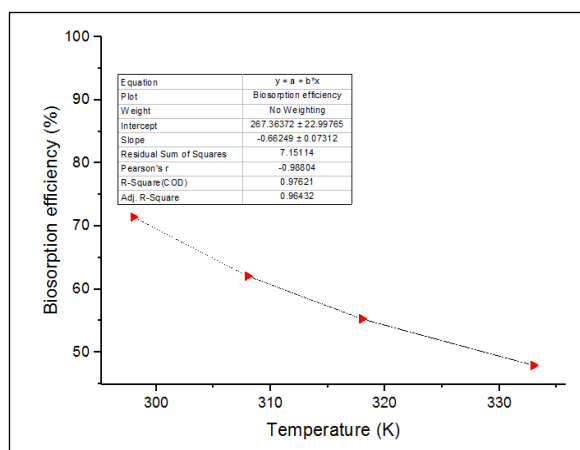


Figure 8. Effect of temperature on the biosorption of mercury onto 1,10-phenanthroline-graft- cell/Filamentous fungi.

3.6 Biosorption Isotherm

Newest isotherm (Hill isotherm) have been evaluated and compared with two common isotherms (Langmuir and Freundlich) to describe the metal ion (Hg^{2+}) binding to the surface of biosorbent. Table 3 represents the isotherm models, nonlinear form, linear form and the plot equations.

3.6.1 Hill isotherm model: The Hill isotherm model suggested adsorption isotherm to designate various adsorbate binding and non-ideal cooperative phenomenon with the ligand binding capability at one site onto macromolecular, influencing different binding sites on the same macromolecular (Foo & Hameed, 2010). The mathematical expression in the Equation (3):

$$q_e = \frac{q_H C_e^{n_H}}{K_D + C_e^{n_H}} \quad (3)$$

where q_e : Milligrams of Hg^{2+} / gram of biosorbent
 C_e : Concentration of Hg^{2+} at equilibrium ($g.L^{-1}$)
 K_D , n_H and q_H are Hill isotherm constants

3.6.2 Langmuir isotherm model: This isotherm model gives a map of homogeneous surface within monolayer bonding and/or of the same strength between *adsorbate* molecules and the adsorbent (Oke et al., 2008). The mathematical expression is summarized in Table 3.

3.6.3 Freundlich isotherm model: The Freundlich isotherm model also applied in this work which describes the heterogeneous binding within multi-layer between adsorbate and the adsorbent (Oke et al., 2008).The mathematical expression is summarized in Table 3.

3.6.4 Sips isotherm model: The sips isotherm model assumed that the integration of both models (Freundlich and Langmuir) and postulating the heterogeneous surface for the adsorption framework. In addition, at high concentration of the solute it proposed of monolayer adsorption capacity and at low concentration of solute absolutely diminishes to multilayer adsorption capacity (Debnath & Ghosh, 2008). The mathematical expression in the Equation (4):

$$\frac{1}{q_e} = \frac{1}{Q_{max} K_s} \left(\frac{1}{C_e}\right)^{\frac{1}{n}} + \frac{1}{Q_{max}} \quad (4)$$

where q_e : Milligrams of Hg^{2+} / gram of biosorbent
 Q_{max} : Maximum adsorption capacity(mg/g)
 K_s and n : Sips isotherm constants
 C_e : Concentration of Hg^{2+} at equilibrium ($g.L^{-1}$)

As shown from Figure 9, the experimental results by observing the R^2 values of the isotherm models, it was found that the Hill isotherm fitted well ($R^2 = 0.9896$) and sips ($R^2 = 0.9863$). However, the Langmuir model ($R^2 = 0.9715$) reasonably fitted the data followed by Freundlich model ($R^2 = 0.9425$).

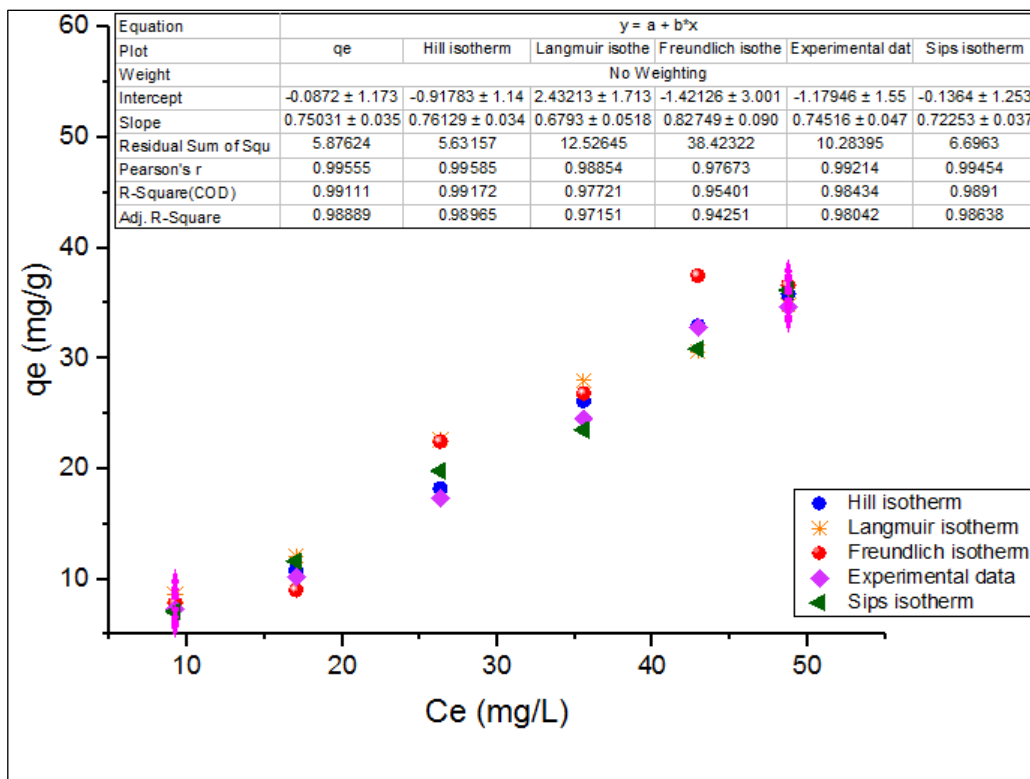


Figure 9. Isotherm models of Hill, Sips, Langmuir and Freundlich

The capacity of Hill and Sips models approved that the homogeneous biosorption on the heterogeneous surface of 1,10-phenanthroline-graft-cell/Filamentous and the cooperative phenomenon of the sorption Hg^{2+} ions. Furthermore, Hill isotherm was superior among the other isotherm models (Adie et al., 2010). The maximum adsorption capacity proposed by Hill model was 78.67(mg/g) and Sips 78.42(mg/g) were lower than Langmuir models which was 85.16(mg/g). Table 4 showed the maximum

adsorption capacity of applied isotherm models and their parameters. In other hand, the equilibrium data almost fitted to the Freundlich isotherm supporting the postulation of heterogeneous shape of biosorption to certain range. On the bases of Langmuir model the biosorption of Hg^{2+} onto 1,10-phenanthroline-graft-cell/Filamentous was in the favourable area and that confirmed by the separation factor ($RL < 1$) (Mittal et al., 2013).

Table 3. Isotherm models and their nonlinear and linear forms

Isotherm	Linear form	Nonlinear form	Plot
Hill	$\log \frac{q_e}{q_H - q_e} = nH \log(C_e) - \log K_D$	$q_e = \frac{q_H C_e^{nH}}{K_D + C_e^{nH}}$	$\log \frac{q_e}{q_H - q_e} \text{ vs } \log(C_e)$
Langmuir	$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o}$ $\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_o C_e}$ $q_e = Q_o - \frac{q_e}{bC_e}$ $\frac{q_e}{C_e} = bQ_o - bq_e$	$q_e = \frac{Q_o b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} \text{ vs } C_e$ $\frac{1}{q_e} \text{ vs } \frac{1}{C_e}$ $q_e \text{ vs } \frac{q_e}{b C_e}$ $\frac{q_e}{C_e} \text{ vs } q_e$
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e \text{ vs } \log C_e$

Table 4. Statically results of isotherm parameters

Models	Parameter	R2
Hill	q _e = 78.67 mg/g K _D = 38.59 n _H = 1.02	0.9896
Sips	q _e = 78.42 mg/g n = 0.93 K _s = 0.02	0.9863
Langmuir	q _e = 85.16 mg/g b = 0.03 RL = 0.28 (RL = 1/1+bCo)	0.9715
Freundlich	n = 1.37 KF = 3.15	0.9425

4. CONCLUSIONS

The evaluations of a new treatment mode for removal of mercury ions from aqueous solutions have been examined. In this work, *Aspergillus* Sp. used as an effective biosorbent and modified by 1,10-phenanthroline, the characterization of FT-IR spectra and SEM analyses confirmed the macro groups grafted successfully on the surface of *Aspergillus* Sp. Nevertheless, solution pH had obvious influences on the biosorption capacity of Hg²⁺ ions and it was found that the biosorption capacity (39.8 mg/g) and biosorption efficiency (R% = 89) at pH equal to 3. In turn, the maximum adsorption efficiency of mercury onto modified *Aspergillus* Sp. was found decrease with rise of temperature due to the fact that the adsorption is an exothermic in nature.

Furthermore, the experimental investigations were performed used most recommended isotherm (Hill, Sips, Langmuir and Freundlich) models in order to control the biosorption capacity, among these applicable models the Hill (R²=0.9896) and Sips (R²=0.9863) models fitted well enough with experimental data followed by Langmuir (R²=0.9715). Thus, the equilibrium data almost fitted to the Freundlich isotherm supporting the postulation of heterogeneous shape of biosorption to certain range.

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