Langmuir and Freundlich Isotherm Studies of Copper (II) Removal using Varıous Adsorbents for Purifying Water

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Abstract: ***Distinctive adsorption equilibria studies are of extensive use in explaining the biosorption of heavy metals, denoting the need to highlight and summarize their essential issues, which is the main purpose of this paper. As a general trend, up until now, most studies on the biosorption of Cu(II) by miscellaneous biosorbent types have been directed toward the uptake of single metal in preference to multicomponent systems. In particular, Langmuir and Freundlich models are the most common isotherms for correlating biosorption experimental data though other isotherms, whichwere initially established for gas phase applications, can also be extended onto biosorption system.***

Keywords: Purification, Copper, Adsorbent, isotherm

1. Introduction

Till recent years, the surge of industrial activities has intensified more environmental problems as seen for example in the deterioration of several ecosystems due to the accumulation of dangerous pollutants such as heavy metals [1]. Heavy metals are still being used in various industries due to their technological importance. Yet, imperfect treatment of waste products from these industries will carry other issues to human health and environment [2]. Aside from the environmental damage, human health is likely to be affected as the presence of heavy metals beyond a certain limit brings serious hazards to living organisms. For instance, cadmium (II), copper(II) and nickel(II) ions (in respective order) have been proven to cause kidney damage, liver damage or Wilson disease [3] and dermatitis or chronic asthma [4] (also in respective order).

Several methods have been employed to remove heavy metal ions from wastewater, which include precipitation, flotation, ion exchange, membrane-related process, electrochemical technique and biological process [2, 5–10]. Low efficiency performance particularly when used on very small concentration of heavy metals, the necessity of using expensive chemicals in some methods as well as accompanying disposal problem are among the drawbacks of these conventional methods [8]. In regards of its simplicity and high-efficiency characteristics even for a minute amount of heavy metals, adsorption is looked upon as a better technology. Activated carbon is a well-known adsorbent and proven to be useful for the removal of heavy metals. Nevertheless, the application of activated carbon for wastewater treatment is not feasible due to its high price and cost associated with the regeneration as a result of high-degree of losses in real process [1].

Removal of heavy metals using agricultural waste and its industrial by-products has been massively investigated due to the abundance of agricultural-related materials in nature and its low cost [11–21]. The use of living and dead microbial cells in biosorption of heavy metals has been demonstrated as well. Several reviews can be referred upon that talk about low-cost adsorbents application for heavy metals removal [4, 22–23]. For example, Kurniawanet al. [4] discussed about the removal performance and cost-effectiveness of various low-cost adsorbents derived from agricultural waste, its industrial by-product as well as natural material. The adsorption capacity of these low cost adsorbent are summarized and compared to those using activated carbon for the removal of heavy metals from metal-contaminated wastewater. Later on, a review about biosorption of precious metals was written by Mack et al. [22]. Their summary paper covers 15 studies on recovery of precious metals using biosorption technique.

Even a number of reviews are already available, which deal with elimination of heavy metals using various kinds of biosorbents. However, by acknowledging the complexity of many factors influencing the process, beside its development and remain increasing number of scientific publications within this area, the already available reviews will not adequately cover all the important aspects in the adsorption process. Hence, this work attempts to summarize recent studies in the removal of heavy metals using biosorbents published between 2007 and early 2019. The emphasis will be on the equilibrium and kinetic aspects of heavy metals adsorption. The main content is the various models used in the adsorption studies. A new aspect on both experimental and theoretical studies is also provided.

2. Equilibrium studies in biosorption of Cu (II) using various kinds of biosorbents

Biosorption of heavy metal is a passive non-metabolically mediated process of metal binding by biosorbent. Agricultural waste and its industrial by-products, bacteria, yeasts, fungi, and algae can be functioned as biosorbents of heavy metals. Biosorption is consideredto be a fast physical/chemical process, and its rate is governed by the type of the process. In another sense, it can also be defined as a collective term for a number of passive accumulation processes which in any particular case may include ion exchange, coordination, complexation, chelation, adsorption and microprecipition.

Proper analysis and design of adsorption/biosorption separationprocesses requires relevant adsorption/biosorption equilibria as one of the vital information. In equilibrium, a certain relationship prevails between solute concentration in solution and adsorbed state (i.e., the amount of solute adsorbed per unit mass of adsorbent). Their equilibrium concentrations are a function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is referred as adsorption isotherm. Several adsorption isotherms originally used for gas phase adsorption are available and readily adopted to correlate adsorption equilibria in heavy metals biosorption. The most widely used among them are Freundlich and Langmuir equations. The application of these isotherms on biosorbent-assisted heavymetals removal from water and wastewater will be discussed in subsequent order.

2.1 Freundlich isotherm

Freundlich isotherm is an empirical equation. This equation is one among the most widely used isotherms for the description of adsorption equilibrium. Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents including biosorbent. This equation has the following form

$$q_e = K_F C_e^{1/n} \quad (1)$$

Eq. (1) can also be expressed in the linearized logarithmic form

$$\log q_e = \log K_F + \frac{1}{n}\log Ce \quad (2)$$

The plot of log qe versus log C_e has a slope with the value of 1/nand an intercept magnitude of log K_F. log K_F is equivalent to log $q_e$when C_e equals unity. However, in other case when 1/n / = 1, the $K_F$value depends on the units upon which qe and $C_e$are expressed. On average, a favorable adsorption tends to have Freundlich constant n between 1 and 10. Larger value of n (smaller value of 1/n) implies stronger interaction between biosorbent and heavy metal while 1/n equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites [24].

Table 1: Freundlich parameters and conditions for adsorption of Cu(II) by various kinds of biosorbents

Biosorbent	Operational condition		Freundlich parameters			Reference
	PH	Temperature (◦C)	K_f(mg/g)	n	R^2	
Green Algae	5	25	1.0252	0.6238	0.9999	[6]
Activated Carbon From Green Algae	5	25	2.8125	0.6402	0.9977	[6]
Natural Fungi Growing On Corncob	5		2.40×10^{-5}	0.59	0.9107	[25]
Maple Wood Sawdust	6	23	0.7439	0.5442	0.9949	[7]
Potassium Hydroxide Treated Pine Cone Powder	5		3.733	2.358	0.994	[9]
Olive Stone	5	25	0.118	1.92	0.859	[12]
Pine Bark	5	25	0.546	1.66	0.932	[12]
Sunflower Hulls	5	30	5.382	0.456	0.947	[14]
Chitosan-Coated Sludge	3-4		1.1293	2.06	0.9379	[16]
Pinus Resinosa	5	30	1.107	2.274	0.9911	[13]
Calcium Pretreated Sawdust	5.6		16.19	2.09	0.927	[18]
Egg Shell	6		2.9403	0.8334	0.999	[19]
Almond Shell	5	20	0.91	2.23	0.97	[17]
Waste Leaves of Kafal	6	30-50	1.629	0.317	0.931	[15]
Water Treatment Sludge	6.6	80	35.5	3.748	0.947	[20]

As a robust equation, Freundlich isotherm has the ability to fitnearly half experimental adsorption–desorption data, and is especially excellent for fitting data from highly heterogeneous sorbent systems as listed in Table 1. Accordingly, this isotherm can adequately represent the biosorption isotherm for some of the systems studied. Forinstance, in the biosorption of Cu(II) using green algaeat PH 5 where correlation valuewas 0.9999 [6].Still, in some cases, Freundlich isotherm could not fit the experimental data well (as pointed by the low correlation values) or not even suitable for the biosorption equilibria expression. This failure is revealed by the value of n which is less than one, as showig of copper removal by waste leaves of Kafal [15].

Apart fromthe ability to representwell in most cases (as shownby high correlation values), a physical meaning of 1/nwas not clear in several studied systems. This is demonstrated in the biosorptionof Cu(II) using natural fungi growing on corncobat pH 5 [6], Maple Wood Sawdust using as biosorbent at pH 6 and 23 °C [7], Cu(II) removal by using potassium hydroxide treated pine cone powder at pH 5 [9], biosorbtion of copper (II) using egg shell at pH 6 [19], biosorbtion by using Pinus Resinosa at pH 5 and 30 °C [13] as well as Calcium Pretreated Sawdust using to removal Cu(II) at pH 5.6 [18]. A 1/nvalue of higher than unity (n less than one) suggests the presence of a concave/curved upward isotherm, sometimes called as solvent-affinity type isotherm [24]. Within this type of isotherm, themarginal sorption energy increases with increasing surface concentration. In this case, strong adsorption of solvent as a result of strong intermolecular attraction within the adsorbent layers occurs. As evidenced in these examples, the adsorption experimental data has the tendency to be in convex rather than concave form. Yet, in specific system studied using the Freundlich model fitting, the obtained parameter n was less than one (please refer to Table 1).

Specifically speaking, the experimental data suggesting a convex isotherm (1/n<1), but Freundlich model gave 1/n>1. Aconcave type of isotherm experimental data of the biosorption of Cu(II) on egg shell [19]. As-depicted irregular pattern of experimental data and isotherm curve represented by Freundlich equation are likely to be caused by the complex nature of the sorbent material and its varied multiple active sites as well as the complex solution chemistry of some metallic compounds.

2.2. Langmuir isotherm

Another widespread-used model for describing heavy metals sorption to biosorbent is the Langmuir model. Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. Table 2 abridges a number of studies that draw upon Langmuir isotherm to interpret biosorption equilibrium data. This isotherm based on three assumptions, namely adsorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy. By applying these assumptions, and a kinetic principle (rate of adsorption and desorption from the surface is equal), the Langmuir equation can be written in the following form:

$$q_e = \frac{q_{max} K_L C_e}{1+K_L C_e} \quad (3)$$

where q_e is the equilibrium amount of metal adsorbed, C_e is the equilibrium concentration of metal ions in the solution, q_{max} is the maximum adsorption capacity or the theoretical monolayer saturation capacity and K_L is the Langmuir equilibrium constant.

Table [2] presents a comparative list of the sorptive capacity of various biosorbents of copper ions(II) The material analysed in literature., sunflower hulls, have a high efficiency at pH 5 and also egg shell has a relatively high capacity at pH 6 as compared to other sorbents mentioned in the relevant literature. Maximum adsorption capacity of these adsorbent were 57.14 mg/g and 48.3 mg/g, respectively. this capacity could be increased by using their pretreated. Consequently the copper ions were adsorbed onto sunflower hulls and egg shell surface in monolayer coverage.

Table 2: Langmuir parameters and conditions for adsorption of Cu(II) by various kinds of biosorbents

Biosorbent	Operational condition		Langmuir parameters			Reference
	PH	Temperature (◦C)	q_{max} (mg/g)	K_L	R^2	
Green Algae	5	25	9.074	0.106	0.9404	[6]
Activated Carbon From Green Algae	5	25	12.484	0.33	0.9352	[6]
Natural Fungi Growing On Corncob	5		1.77	6.92×10^{-4}	0.8816	[25]
Maple Wood Sawdust	6	23	9.191	0.044	0.9294	[7]
Potassium Hydroxide Treated Pine Cone Powder	5		26.32	0.0542	0.943	[9]
Olive Stone	5	25	1.965	0.0208	0.961	[12]
Pine Bark	5	25	11.935	0.247	0.983	[12]
Sunflower Hulls	5	30	57.14	0.029	0.994	[14]
Chitosan-Coated Sludge	3-4		18.83	0.58	0.9994	[16]
Pinus Resinosa	5	30	10.94	0.063	0.9984	[13]
Calcium Pretreated Sawdust	5.6		37.74	0.91	0.996	[18]
Egg Shell	6		48.3	0.9358	0.9934	[19]
Almond Shell	5	20	6.64	0.08	0.98	[17]
Waste LeavesOf Kafal	6	30-50	6.849	4.219	0.950	[15]
Water Treatment Sludge	6.6	80	35.00		0.903	[20]

3. Conclusion

The equilibrium adsorption isotherms are one of the most fundamental data to comprehension the mechanism of the adsorption systems. Langmuir and Freundlich isotherm are the two most mighty used models for describing the equilibrium. The difference between both models has been a substantail. The Freundlich isotherm was empirical construct , while Langmuir's model is a theoretic. Assumed in the Langmuir model, that at maximum coverage, there is only a single layer of molecules on the surface and no further stacking of adsorbed molecules.

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