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Marine Algae Bioadsorbents for Adsorptive Removal of Heavy Metals

Mazen K. Nazal

Abstract

With the shortage of freshwater resources and as wastewater output of huge industries as well as pollution that might be happening in the ecosystem, wastewater treatment is of utmost importance. Removal of pollutants such as heavy metals from wastewater would provide an exceptional alternative water resource. Extensive research has been done to develop an operative technology to overcome the toxicity and the negative environmental impact of heavy metals and their ionic forms. In this book chapter, biomass bioadsorbents utilizing marine algae for adsorptive removal of heavy metal pollutants from wastewater were discussed. The most common adsorption isotherms and kinetic models, which used to study their nature of adsorption, were also covered.

Keywords: macroalgae, adsorption isotherm, adsorption kinetics, wastewater, adsorbents

1. Introduction

1.1 Wastewater

Water which is the key element responsible for life in the world is becoming more valuable due to the increased consumption and demand. In order to provide a locally controlled water supply, wastewater recycling offers great environmental advantages. Recycling of water can corporate in decreasing the consumption of water from sensitive ecosystem, reducing the environmental pollution, and even preventing accumulation of pollutants in our ecosystem. The US Environmental Protection Agency (USEPA) has suggested three stages of water recycling; in the primary stage that can be achieved by a sedimentation process, normally the produced water is not suitable for any use. The biological oxidation and disinfection process are used to reach the secondary stage. The produced water from that stage can be used mainly for irrigation of nonfood crop and industrial cooling system. The tertiary stage in wastewater treatment is reached using chemical, coagulation, filtration, and disinfection processes. Produced water in the tertiary stage can be employed mostly for irrigation of food crops and landscape, washing of vehicles, and flushing toilet [1]. Good quality water (i.e., water free of contaminants) is essential to human health and a critical feedstock in a variety of key industries including oil and gas, petrochemicals, pharmaceuticals, and food. The available supplies of water are

decreasing due to (1) low precipitation, (2) increased population growth, (3) more strict health-based regulations, and (4) competing demands from a variety of users, e.g., industrial, agricultural, and urban development. In addition, our water today became such type of cocktail of chemicals that has more than 100 of toxic compounds, viruses, bacteria, and metals. Consequently, water scientists and engineers are seeking alternative sources of water and new technologies for wastewater treatment and recycling. These wastewaters include but not limited to sewage effluent, contaminated surface or groundwater, and industrial wastewater. Water recovery-recycle-reuse has proven to be effective and successful in creating a new and reliable water supply while not compromising public health [2].

1.2 Heavy metals

Water pollution with contaminants became a global issue. Among of these contaminants, heavy metals have a greater concern mainly due to their bioaccumulation, toxicity, and non-biodegradability. Their non-biodegradability nature makes their existence in water to cause great risk to living organisms. Accordingly, many government environmental agencies such the US Environmental Protection Agency (USEPA) and World Health Organization (WHO) have set the maximum acceptable concentration level for heavy metals in recycled water. Therefore, different methodologies, with varying level of success, have been employed to remove these contaminations from water and wastewater. Biological treatment (aerobic and anaerobic), coagulation, precipitation, oxidation, membrane, and filtration are common methods of removing microorganisms and ionic and cationic compounds from wastewater streams. The performance of these methods is generally acceptable at low concentration of heavy metals below few hundred ppm, which is the main drawback of them. Even though most of the wastewater treatment technologies available today are effective, they are often costly and time-consuming methods. Bioadsorption is considered as among the most promising low-cost process for wastewater treatment. Numerous materials were used as adsorbents to remove heavy metal ions from water, such as metal oxides, activated carbon, zeolite, chitin, metal sulfide, resin, etc. The search for new and more effective materials to be used as bioadsorbent materials has a continuous effort and been considered by many researchers. Since 1990 till now, there are more than 5000 publications in the field of bioadsorption of heavy metals, and approximately 6% of these publications have been concerned on using marine algae [3]. **Figure 1(a and b)** shows the dramatic increase in both the number of publications and their citations versus time.

1.3 Marine algae

Marine algae are one of the most highly available natural resources in tropical ecosystem where around 2 million tons of them are collected from seas and oceans and cultured in artificial system [4]. They are useful in different applications such as pharmaceutical, food, and cosmetic industries. Algae have rich biochemical composition; therefore, its biomass is a promising material to be used as bioadsorbent to decontaminate water and wastewater by removing pollutants such as heavy metals [5, 6]. Marine algae are commonly known as seaweeds, and they had a great potential to be used in pollutant removal process as a promising bioadsorbents material. This is due to their renewable availability, distinct properties, and high biosorption capacity. Seaweeds are divided into three main broad groups, namely, (i) green (Chlorophyta), (ii) red (Rhodophyta), and (iii) brown (Phaeophyta) algae. Marine algae have many advantages for bioadsorption. Among them brown algae provided the best adsorption capacities due to their cell wall structure and components.

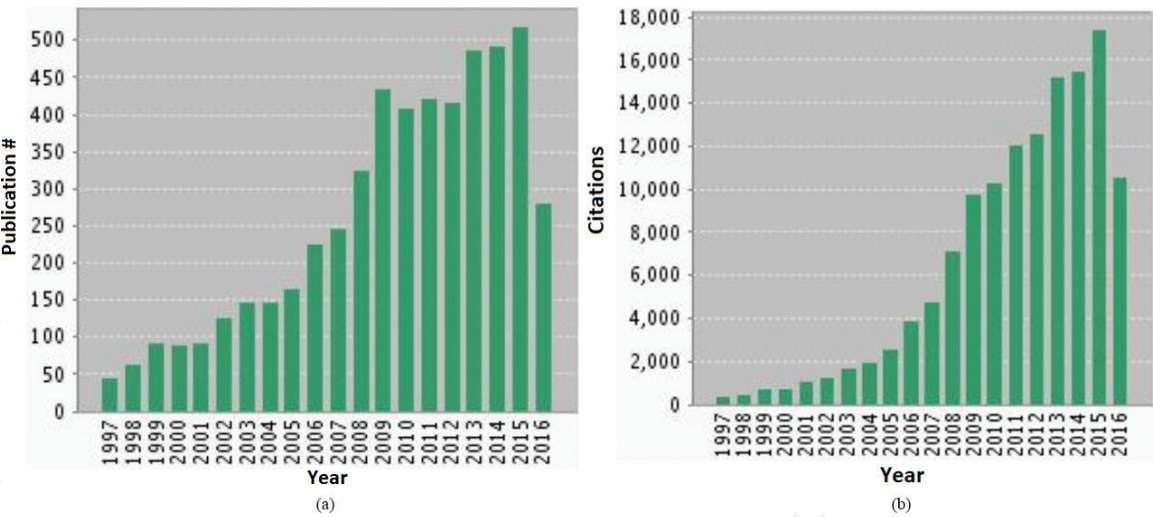


Figure 1. Histograms for (a) number of publications in the field of biosorption of heavy metals and (b) the number of citations each year on these publication [3].

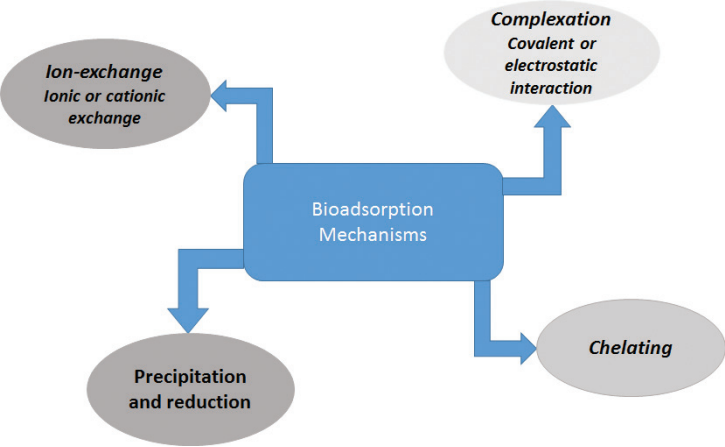


Figure 2. Classification of metal uptake mechanism by bioadsorbents.

The cell wall of brown algae has a lot of active chemical functional groups such as hydroxyl, carboxylic acid, amine, imidazole, phosphate, phenolic, thioether, and sulfhydryl which offer a selective binding and interaction with metals and pollutants in the bioadsorption process. It contains mainly cellulose, a group of salts of sodium, potassium magnesium, and calcium, and alginate, which is a type of polysaccharide (anionic copolymer) [7].

Figure 2 illustrates the main four mechanisms of heavy metal uptake by bioadsorbents. The first one is ion-exchange process including ionic or cationic exchange. The surface of the cell wall contains mainly organic nitrogen group in the case of ionic exchange or hydroxyl and organic sulfate or phosphate in the case of cationic exchange. The uptake mechanism can be a complexation through a covalent or electrostatic interaction where the metal ions form a complex compound with organic molecules. The third mechanism is chelation which involves an interaction between the metal and an organic compound that has more than one electron donor functional group. The last one is through precipitation that occurs when the pH of the solution varies due to cellular metabolism or when the concentration of metals increases [8].

Table 1 summarizes some of the marine algae (red, green, and brown), those used for removal of transition, actinide, or lanthanide metals. Many researchers found that the *Sargassum* brown algae has a high adsorption capacity

Number	Name of algae	Removed metals	Ref.
1	<i>Sargassum</i> sp.	Cu	[9]
2	<i>Sargassum</i> sp.	Sm and Pr	[10]
3	<i>Spirogyra</i> spp.	Cr	[11]
4	<i>Sargassum vulgare</i>	Cd and Ni	[12]
5	<i>Sargassum hystrix</i>	Pb	[13]
6	<i>Sargassum natans</i>	Pb	[13]
7	<i>Sargassum hemiphyllum</i>	Ni and Cu	[14]
8	<i>Sargassum wightii</i>	Ni	[15]
9	<i>Sargassum</i> sp.	Cr	[15]
10	<i>Sargassum honeri</i> and <i>S. hemiphyllum</i>	Ho, Dy, Lu, and Yb	[16]
11	<i>Sargassum ilicifolium</i>	Ni and Co	[17]
12	<i>Sargassum</i> sp.	La, Nb, Eu, and Gd	[18]
13	<i>Sargassum muticum</i> and <i>Fucus spiralis</i> (brown algae)	Pd, Zn, and Cd	[19]
14	<i>Fucus vesiculosus</i> (brown algae)	Cu	[20]
15	<i>Palmaria palmata</i> (red algae)	Cu	[20]
16	<i>Fucus spiralis</i> (brown algae)	Cu	[20]
17	<i>Ulva</i> sp. (green algae)	Cu	[20]
18	<i>Fucus ceranoides</i> and <i>Fucus serratus</i> (brown algae)	Cd	[21]
19	<i>Laminaria japonica</i>	Cd, Pb, and Fe	[22]
20	<i>Laminaria japonica</i> (washed or oxidized by potassium permanganate)	Pb	[23]
21	<i>Gracilaria fischeri</i>	Cu and Cd	[24]
22	<i>Gracilaria</i> sp.	Cd, Cu, Zn, Pb, and Ni	[25]
	<i>Padina</i> sp.	Cd, Cu, Zn, Pb, and Ni	[25]
23	<i>Pilayella littoralis</i>	Cr, Fe, Al, Cd, Cu, Zn, Co, and Ni	[26]
24	<i>Cladophora crispata</i>	Pb, Cu, Cd, and Ag	[27]
25	<i>Cladophora fascicularis</i>	Cu and Pb	[28]
26	<i>Ecklonia</i> sp.	Cr	[29]
27	<i>Colpomenia sinuosa</i>	Ni and Cu	[14]
28	<i>Petalonia fascia</i>	Ni and Cu	[14]
29	<i>Ulva fascia</i>	Ni and Cu	[14]
30	<i>Padina pavonica</i>	Ni and Cd	[12]
31	<i>Sargassum cymosum</i>	Cr	[30]
32	<i>Turbinaria conoides</i>	Pb	[31]
33	<i>Laurencia obtusa</i>	Cd, Co, Cr, Cu, and Ni	[32]
34	<i>Ulva reticulata</i>	Zn	[33]
35	<i>Ascophyllum nodosum</i> <i>Fucus spiralis</i> <i>Laminaria hyperborean</i> <i>Pelvetia canaliculata</i>	Cu, Ni, Zn, and Ca	[34]

Table 1.
Marine algae used in bioadsorption removal of heavy and lanthanide metals.

to remove heavy metals such as Cu, Ni, Cd, Pd, Cr, Sm, and Pr from their solution efficiently due to its cell wall structure that is rich in active bioadsorption sites [9, 10, 15, 17–19]. Mostly, bioadsorption offers many advantages over the bioaccumulation process since bioadsorbents are available commonly as by-product or waste, as well as they do not need growth media and growth conditions. As a result, they are considered low-cost materials with high possibility to be reused for many cycles. The literatures show that marine algae can be used for the removal of heavy metals in dead or live forms. However, in industrial applications, the nonliving marine algae provide more practical bioadsorbent materials for the removal of pollutants. This is because toxicity of heavy metals and other pollutants do not affect dead biomass. In addition, the performance of those bioadsorbents can be improved by physical treatments such as heating or chemical processing such as acid or base treatments. This enhancement in their biosorption capacity is attributed to activation of the adsorption sites as well as rearrangement of the cell wall structure to be more accessible and compatible for pollutants capturing and removal [35].

2. The nature and kinetics of bioadsorption

2.1 Adsorption isotherm models

An idea about the adsorption process is predicted using the correlation between the pressure or the concentration of adsorbate and the adsorption capacity (X/m) at constant temperature as shown in **Figure 3**.

The amount of adsorbate (X) adsorbed should be normalized by the mass of adsorbent (m) to allow comparison of different materials. From **Figure 1**, it can be predicted that after the saturation point, the number of adsorption sites on the adsorbent is occupied, and the vacancies became limited so that the adsorption does not occur anymore. There are five general types of adsorption isotherms. They are as follows:

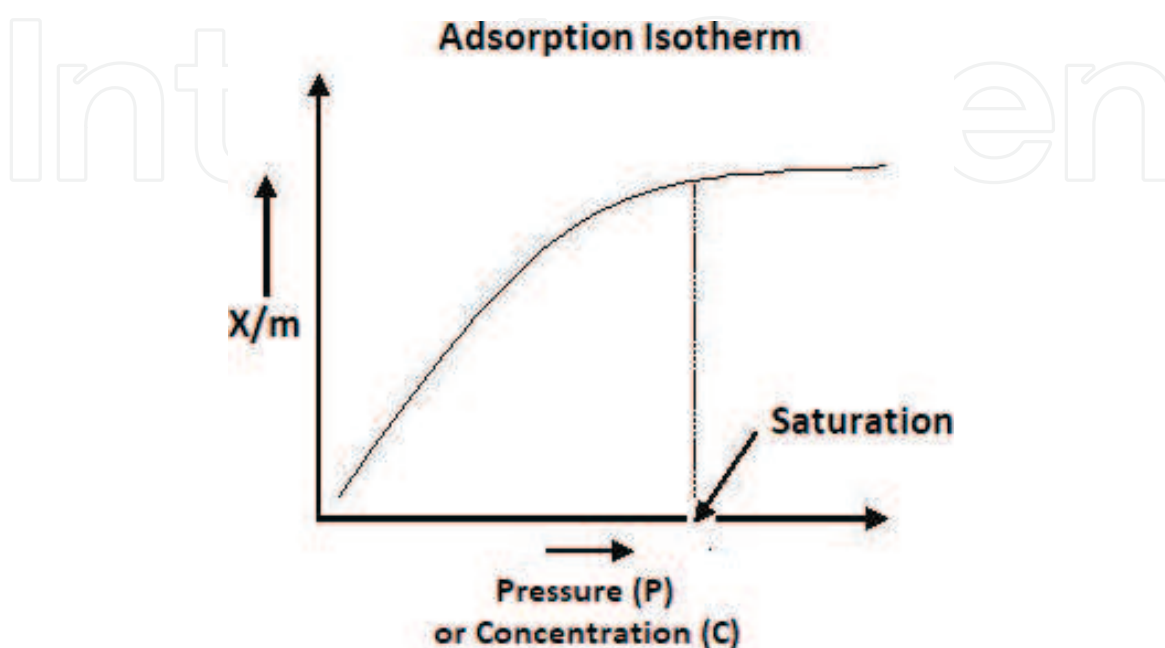


Figure 3.
Adsorption isotherm.

- Type I adsorption isotherm (shown in **Figure 2**)

The main characteristics of this type are (i) there is a monolayer adsorption and (ii) it might be explained using the Langmuir adsorption isotherm.

- Type II adsorption isotherm

Figure 4 shows a typical adsorption isotherm curve of type II. This type of adsorption shows a large deviation from the Langmuir isotherm model and a flat region, which is corresponding to a monolayer formation.

- Type III adsorption isotherm

This type of isotherm indicates that there is no flat region as shown in **Figure 5**, and also there are formations of multilayer adsorption.

- Type IV adsorption isotherm

It can be depicted from **Figure 6** that there is a monolayer formation (intermediate region), which is followed by a multilayer formation at certain adsorbate concentration. At low concentration of adsorbate, the adsorption is mostly similar to type II adsorption isotherm.

- Type V adsorption isotherm

It is similar to type IV with a difference in the range of adsorbate's concentration where the monolayer and multilayer start the formation as shown in **Figure 7**.

The adsorption isotherms usually are being studied to understand the adsorption behavior modulation and to calculate the adsorption capacity for the adsorbents, so the data analysis is done using a linear/nonlinear least squares methods of adsorption isotherms, where they describe the relationship between the adsorbed amount of adsorbate and its equilibrium concentration in the solution.

The Freundlich, Langmuir, Temkin, Sips, and Redlich-Peterson models are the most common types of the adsorption isotherms to describe the metal ion bioadsorption from their single component solution.

The Freundlich isotherm (Eq. 1) is an empirical model where the adsorption occurs on heterogeneous adsorption sites on adsorbent surface, which is the general case in macroalgae bioadsorbents:

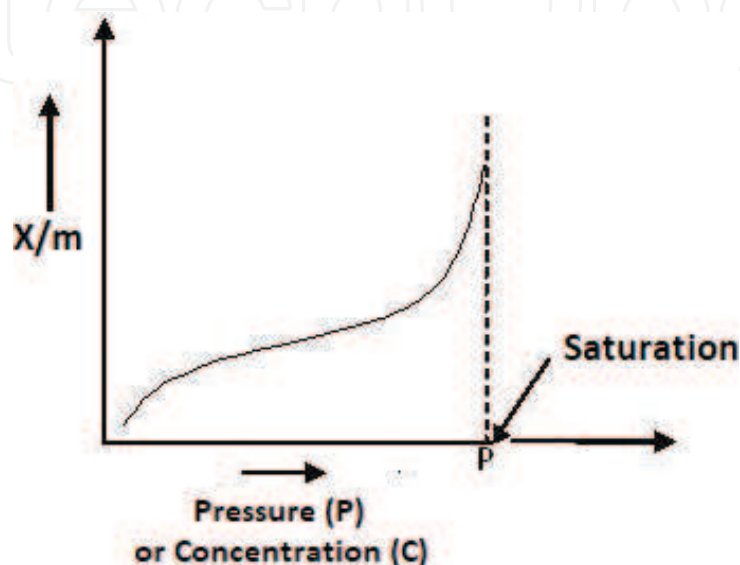


Figure 4.
Type II adsorption isotherm.

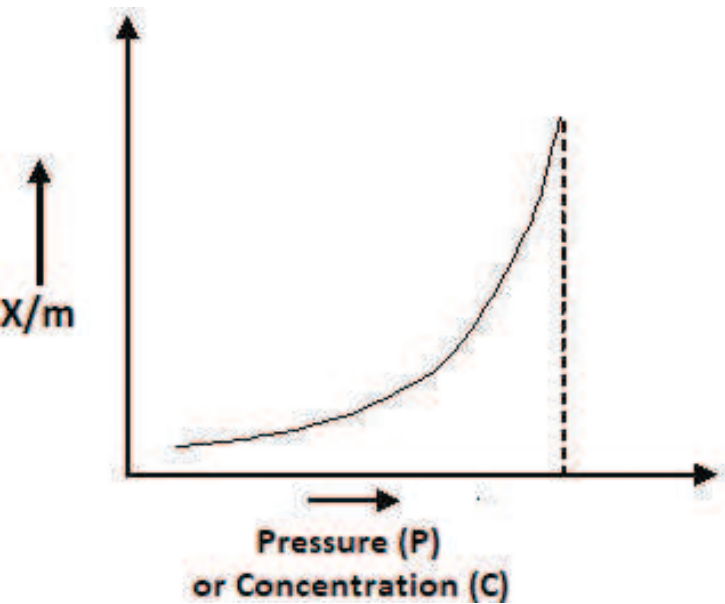


Figure 5.
 Type III adsorption isotherm.

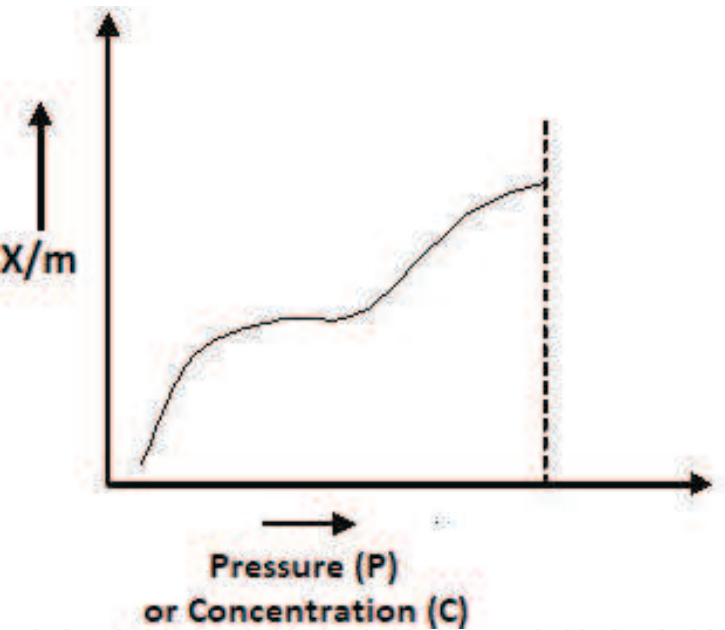


Figure 6.
 Type IV adsorption isotherm.

$$q_e = K_f C_e^{1/n} \tag{1}$$

where

- q_e : The adsorption density at equilibrium (mg adsorbate/g of adsorbent).
- C_e : The residual adsorbate concentration in the solution (mg/L) at equilibrium.
- K_f : The relative adsorption capacity ($\text{mg}^{1-1/n} \text{L}^{1/n} / \text{g}$).
- n : The unit less constants reflect the adsorption intensity.

A plot of $\ln C_e$ against $\ln q_e$ will give a straight line with a slope $1/n$ and intercept $\ln K_f$. Smaller $1/n$ greater expected heterogeneity [35]. It is worthy here to note that usually the adsorption data have a good fit with the Freundlich isotherm model due to the well-known insensitivity of its linear form (ln-ln plot).

The Langmuir adsorption isotherms model is considered as the best known for describing a monolayer chemical adsorption process on homogenous adsorption

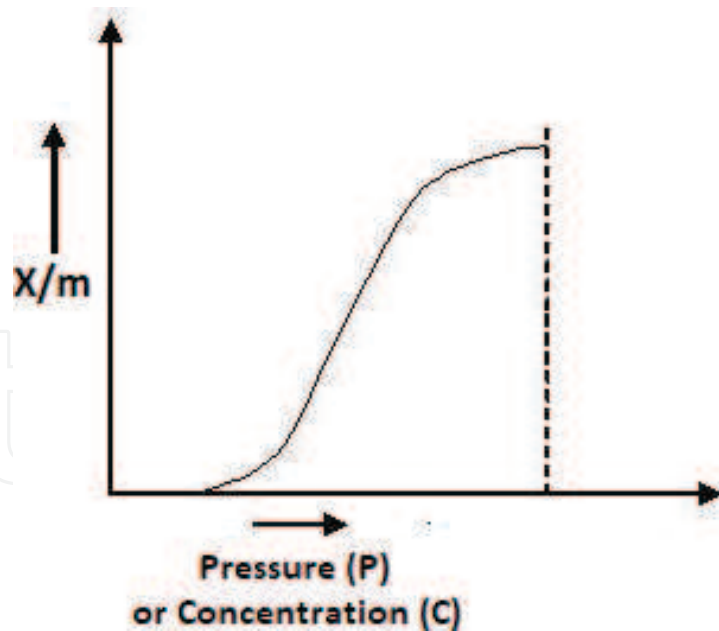


Figure 7.
Type V adsorption isotherm.

sites on adsorbent surfaces. It partially considers the thermodynamic in the adsorption process. It is expressed in Eq. (2):

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

where

q_e : The adsorption capacity at equilibrium (mg of adsorbate/g of adsorbent).

C_e : The residual adsorbate concentration at equilibrium in solution (mg/L).

q_{max} : The maximum adsorption capacity corresponding to monolayer coverage (mg of analyte adsorbed/g of adsorbent).

b : The Langmuir constant correlated to the adsorption energy (1/mg adsorbate).

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L (Eq. 3), which is a dimensionless constant referred to as separation factor or equilibrium parameter [36]:

$$R_L = \frac{1}{1 + (1 + K_L C_e)} \quad (3)$$

The most used linear form of the Langmuir model is the following form (Eq. 4), which is also called reciprocal Langmuir plot:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (4)$$

Plotting C_e/q_e versus C_e from the experimental data gives a linear regression where the slope for that plot gives the experimental maximum adsorption capacity q_{max} , and the intercept gives the Langmuir constant b .

There are another three linear transformation forms of the Langmuir isotherm models: (1) the distribution coefficient or Scatchard plot, (2) Eadie-Hofstee plot, and (3) double reciprocal Lineweaver-Burk plot. Every one of these four linear transformation forms gives a greater weighing to low adsorption values than to high adsorption values, which leads to changing in the error distribution [37].

The energy of adsorption can be described using the Temkin isotherm (Eq. 5). However, this isotherm is valid only for an intermediate range of adsorbate concentrations [38]:

$$q_e = \frac{RT}{b} \ln (A_T C_e) \quad (5)$$

Rearranging Eq. (4) results in Eq. (6):

$$q_e = \frac{RT}{b} \ln (A_T) + \frac{RT}{b} \ln (C_e) \quad (6)$$

Plotting q_e versus $\ln(C_e)$ gives a linear regression where the slope for that plot gives the Temkin isotherm constant (b) and the intercept gives the Temkin isotherm equilibrium binding constant (A_T) (L/g), where R is the universal gas constant (8.314 J/mol K), T is the temperature in Kelvin (K), and B in Eq. (7) is a constant related to heat of adsorption (J/mol):

$$B = \frac{RT}{b} \quad (7)$$

The Sips isotherm model for mono-component system is a combination between the Freundlich and Langmuir isotherm models. Eq. (8) expresses the Sips model:

$$q_e = \frac{q_{max} (b C_e)^{ns}}{(1 + (b C_e)^{ns})} \quad (8)$$

where

q_e : The adsorption capacity at equilibrium (mg of adsorbate/g of adsorbent).

C_e : The residual adsorbate concentration at equilibrium in solution (mg/L).

q_{max} : The maximum adsorption capacity corresponding to monolayer coverage (mg of analyte adsorbed/g of adsorbent).

b : The Langmuir constant correlated to the adsorption energy (1/mg adsorbate).

ns : The Sips constant for the heterogeneity of binding surface.

As an extension for the Langmuir isotherm, a model with three parameters was established expressed in Eq. (9). That is Redlich-Peterson isotherm:

$$q_e = \frac{a_{RP} (C_e)}{(1 + (b_{RP} C_e^{n_{RP}}))} \quad (9)$$

where C_e (mg/L) is the residual adsorbate concentration at equilibrium in the solution and q_e (mg/g) is the adsorption capacity at equilibrium. However, a_{RP} (1/g) and b_{RP} (1/mg)^{n_{RP}} do not have physical or chemical meaning. The third parameter n_{RP} is dimensionless that gives an idea about the heterogeneity of adsorption sites on the surface of adsorbents [39].

2.2 Kinetic models

Studying the uptake rate of heavy metals is achieved by the adsorption kinetics where the metal ion uptake rate clearly controls residence time of these compounds at the solid-liquid interface, so and in sequence the mechanism of heavy metal adsorption on the biomass materials will be evaluated using the most common kinetic models.

The simplest one which expresses on the proportionality between the metal adsorption and the number of vacant adsorption sites on the surface of adsorbents

is Lagergren model (pseudo-first-order). The nonlinear and linear forms of the model are represented in Eqs. (10) and (11), respectively [40]:

$$q_t = q_e(1 + e^{-k_1 t}) \quad (10)$$

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (11)$$

where q_t and q_e (mg/g), respectively, are the adsorption capacity at any time (t) and at equilibrium. k_1 (1/min) is the pseudo-first-order rate constant.

The kinetic model that has the correlation between the adsorption of metal ions and the square of active vacant adsorption sites on the surface of adsorbents is called pseudo-second-order rate model (Eq. 12) [38]:

$$q_e = \frac{q_e^2(k_2 t)}{(1 + (k_2 q_e t))} \quad (12)$$

Eq. (8) can be rearranged to be in the following linear form (Eq. 13):

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (13)$$

where q_t and q_e (mg/g), respectively, are the adsorption capacity at any time (t) and at equilibrium. k_2 (g/mg min) is the pseudo-second-order rate constant.

By plotting $\ln(q_e - q_t)$ versus t and t/q_t versus t in the previous equations (Eqs. (11) and (13)), all the adsorption kinetic parameters can be determined from the slope and the intercept.

The influence of mass transfer resistance on binding metal ions on adsorbents was tested using the intra-particle diffusion model (Weber and Morris model) represented in Eq. (14) [41]:

$$q_t = k_{id} t^{0.5} + C \quad (14)$$

where q_t (mg/g) is the adsorption capacity at any time (t), k_{id} (mg/g min^{0.5}) is the intra-particle diffusion rate constant, and C (mg/g) is a constant related to the thickness of the boundary layer. From plotting of q_t versus the square root of t , the diffusion constant k_{id} can be calculated. If this plot passes through the origin, then intra-particle diffusion is the only rate-controlling step.

3. Conclusion

Removal of heavy metals from wastewater would provide an exceptional alternative water resource. Algae biomass adsorbents, which utilized for adsorptive removal of heavy metal pollutants from wastewater, show a promising alternative. Different empirical isotherm models for single analyte have been discussed (i.e., Freundlich, Langmuir, Temkin, Sips, and Redlich-Peterson). In a large number of studies, the Freundlich and Langmuir models are the most commonly and widely used isotherm models. The two kinetic models, which are still in a wide use for studying the rate uptake of heavy metals and their bioadsorption from aqueous solutions, are pseudo-first- and pseudo-second-order kinetic models. In chemisorption process, the pseudo-second-order kinetic model is superior to pseudo-first-order model as it takes into account the interaction of adsorbent-adsorbate through their valency forces.

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Conflict of interest

The author declares that there are no conflicts of interest.

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