Macrophytes: A Potent Bio - Sorbent for the Sequestration of Heavy Metals

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Abstract: During the last two decades, several methods have been applied for the treatment of metal bearing wastewater; none of the method was suitable for the industrial purposes due to various drawbacks. Biosorption has introduced a new dimension for the sequestration of heavy metals in the wastewater. The eco –friendliness and cost effectiveness are the added advantage of this technique. A good number of biosorbents have been tried by several researchers for the recovery of metals from the aqueous solution out of which seaweeds is gaining much attention. The intention of this review paper is to highlight the extrapolative nature of seaweeds in the biosorption of heavy metals. Sea weeds are splendidly obtainable resources throughout the world which can be exploited without any expenditure for the treatment of metal contaminated wastewater. This article summarizes the past achievement and present scenario on the seaweed, the most promising biosorbent. The adsorption isotherm models and kinetics are also discussed in this paper which would facilitate one to understand the rate and metals adsorption capacity of the biosorbents, particularly the seaweeds.

Keywords: Biosorption, Sea weeds, algae, water, heavy metals, kinetics, modeling.

1. INTRODUCTION

Water is the most essential constituent for the survival of the living beings in the earth. It is estimated that globally only 2.8% of freshwater is available, the remaining is present in the form of salt water. This meager amount of fresh water even polluted in various ways by a range of hazardous materials. Thereby, the quantity of fresh water availability is decreasing day- by - day. Consumption of the polluted water creates dreadful health oriented disease. Overconsumption leads to fatality. Heavy metal is one among the water contaminating pollutant released by various industries. These metals are continuously released by the industries for an indefinite period which gets accumulated in the food web, and causes a serious impact to the environment. So these effluents have to be treated or else it may have adverse effects on living beings and also to the environment. There are several techniques for the treatment of the metal bearing effluent. Ion – exchange [1], electrochemical oxidation methods[2], precipitation [3], Ion Exchange, Activated carbon, Electrolysis and reverse osmosis [4] are some of the methods for the treatment of wastewater. However, these methods need large quantity of chemicals bring down the metal concentration to a favorable level mean while these methods generate large quantities of sludge and the cost of operation is quite expensive [5, 6]. Biosorption is another method which has gained importance among the environmental researchers. Biosorption is a reversible binding process. The metal ions that are present in the aqueous solutions will get rapidly bounded onto the surface of biomass via functional groups. Biosorption is a surface phenomenon; hence the cellular metabolism has no role in this process whereas the surface molecules play vital part in the sorption of metal ions [7]. Generally,

biosorption can be operated with less capital investment. So, it is a cheap and economical waste water treatment method. Indeed biosorption is quite inexpensive process because ease of use of the biological materials that are normally low-cost and such materials can be easily obtained from the agro waste products [8]. The inherent potential of various biosorbents have been studied profoundly by several invigilators. Seaweeds are proved to be the most excellent biosorbent for the removal of heavy metals from the waste water. These seaweeds come under the broad classification of algae. The algal biology has been broadly classified in microalgae and macro algae. Particularly, macroralgae (Seaweeds) is supposed to have a predominant adsorptive behavior. These macrophytes are flourished largely in the shallow coastal areas also present in the many parts of the oceanic parts of world.

This review is to summarize and illustrate the potential behavior of naturally available seaweed as a biosorbent for the removal of heavy metals from the aqueous solutions. The various modification of the biosorbent has been briefly discussed. In addition the various analytical techniques applied to biosorbent experimental studies. Furthermore the equilibrium isotherm models, Biosorption kinetics and intra-particular diffusion models have also been reviewed.

2. ALGAL BIOSORPTION

The study of algae is called as Psychology. In Greek terminology phykos means alga. The history of psychology has originated right from the beginning of botanical science. The biomass of algae has an excellent biosorptive property and they are selective in nature [9, 10]. The sequestration of heavy metals can be done by

dead algal biomass. Particularly, macro-algae is supposed to have a predominant adsorptive behavior. The three main groups of macro algae are red algae, green algae and brown algae. These algal materials shown to have superior properties and so they are significantly used in the removal of heavy metals. Among these brown algae has peculiar property such as rich functional groups and reusability for several cycles of adsorption.   As mentioned above it is 100 % due to the rich availability of the functional groups in the biomass. Basically the carbon chain forms backbone for the bio-molecules. Each and every bio-molecule holds a functional group. In the case of algae/ seaweeds, there is a rich of functional moieties. The chelating property of the functional groups in biomaterials favors the improved affinity towards the heavy metal ions. In addition to the above-mentioned natural biosorbents, in the literature, some of the natural biosorbents are listed below which have gained significant role in the removal of metal contaminated waste water.

3. SEAWEEDS AND THEIR BIOSORPTION BEHAVIOR

Table.1 List of macro algae used in the biosorption of metals

Macro algae	Sorbate used	References
Ascophyllumsp.	Pb, Cd	[12]
Cladophoracrispata	Cd, Pb, Cu, Ag	[13]
Cladophorafascicularis	Pb	[14]
Codiumfragile	Cd	[15]
Colpomeniasinuosa	Cu, Ni	[16]
Corallinaofficinalis	Cd	[17]
Eckloniasp.	Cr	[18]
Fucus vesiculosus	Cd, Zn, Pb, Cu	[19], [20], [21]
Fucusceranoides	Cd	[19]
Fucus serratus	Cd	[19]
Fucusspiralis	Cu	[20]
Gracilaria fischeri	Cd, Cu	[22]
Gracilariasp.	Pb, Cu, Cd, Zn, Ni	[23]
Janiarubrens	Pb	[24]
Laminariadigitata	Cd, Zn, Pb, Cu	[21]
Laminariajaponica	Cd, Cu, Pb	[25], [26], [27]
Laurenciaobtusa	Cr, Co, Ni, Cu, Cd	[24]
Padinapavonia	Cd, Ni	[28]
Padinasp	Cd	[29]
	Pb, Cu, Cd, Zn, Ni	[23]
	Cu	[29]
Palmariapalmata	Cu	[20]
Petalonia fascia	Cu, Ni	[16]
Pilayellalittoralis	Al, Cd, Co, Cr, Cu, Fe, Ni, Zn,	[30]
Porphyracolumbina	Cd	[15]
Sargassum asperifolium	Pb	[24]
Sargassum hemiphyllum	Cu, Ni	[16]
Sargassum vulgaris	Cd, Ni	[28]
Ulvalactuca	Pb	[24]
Ulvareticulata	Zn	[31]

The seaweed collected from the ocean is known to have an impressive biosorption capacity [11]. The industrial need for the recovery of the metals has made an attempt to examine the metal uptake capacity of each and every biosorbents. The occurrence of iron in the solution is not a major problem even then it may affect the target metal uptake during biosorption. The presence of cadmium in the water is highly toxic so it is to be recovered because of the tremendous discharge in the environment. Table.1 presents the application of various brown algae in the removal of heavy metals.

4. MECHANISMS OF HEAVY METAL UPTAKE BY MACRO ALGAE

It is essential to know the mechanism of biosorption for exploiting the successful development of biosorbents. The main mechanism behind the metal uptake is ion – exchange where there is an exchange of protons and heavy metals at the binding site of the particular sorbent. [19, 32], the other various mechanisms are adsorption by physical forces, electrostatic interactions [33], chelation, complexation [7], and micro precipitation [34]. The main components present in the cell wall such as alginates and fucoidans are responsible for metal uptake [7]. Brown algae, contains high amount of such polysaccharides which added advantage for the higher metal uptake compared to other algae [19]. The alginic acid content in Sargassum [7] is listed in the Table.2

Table.2: Alginic acid contents of Sargassum

Sargassum species	Alginic acid (Percents of dry weight)
Sargassum longifolium	17%.
Sargassumwightii	30%
Sargassum tenerium	35%
Sargassum fluitans	45%
Sargassum oligocystum	≈45%

4.1 Ion exchange
Ion exchange is the principal mechanism for the algal biosorption [19, 22, 28]. Generally, the raw biomass contains light metals ions such as K^+, Na^+, Ca^{2+}, Mg^{2+}, which bound to the acid functional group of alga. Da Costa et al., 2003 have developed a lab scale column to study the release of light metals from stipes and blades of Sargassum sp. in order to evaluate the biosorption of Zn metal uptake [35]. It was found that stipes had a higher light metals compared to that of blades. Therefore, they concluded that the zinc uptake was due to the alkaline and alkaline – rare earth elements.

4.2 Coordination or complex formation
Complex formation is also a kind of mechanism for the metal biosorption. The electrostatic forces and covalent bonds which tightly link the functional groups which adhered to the cell surface of the biomass. For Example in the biosorption of copper by Chlorella vulgaris, there is a rigid co- ordination bond is formed between the functional group such as amino and carboxyl groups of the biomass the metal ion [36].

4.3 Chelation

Generally an organic molecule contains more than one functional group with donor electron pairs can concurrently contribute these to a metal atom. Chelation is the formation of ring structure involving a metal atom. In general, the chelating agent may bond to a metal ion in more than one place simultaneously. Particularly, the chelated compounds are more stable than complexes involving monodentate ligands. When there is a large number of chelating sites in the ligand the stability also increases. Thus, there is a formation of stable metal species by the chelation of metal by ligands of the biopolymer.

5. SEAWEEDS: NATURE AND METAL BINDING CHARACTERISTICS

The potential metal uptake behavior of algal seaweeds has encouraged the researchers to overcome the challenges in the heavy metal removal from the industrial waste water. The ligands in the sea weeds form an ionic interaction with cationic metals in the aqueous solutions, is the basic mechanism behind the binding [37]. Table.3 summarizes various binding groups of brown algae [28]. This technology perhaps follows any one of the following mechanism: ion-exchange, adsorption, complexation and precipitation. Indeed depending upon the nature and type of the biomass the uptake level may vary in addition the mechanism may also diverge. In biosorption either one or two of the above mechanism may occur [38].

6. SEA WEEDS AND ITS ACCOMPLISHMENTS

The scale up of the biosorption for the continuous water treatment may utterly depend on the highly efficient and selective metal binding materials are used even though many biological are obtainable. The success rate of biosorption is only based on the selection of the material capable to do the task in an extreme manner. The material is said to be good not only by its adsorption behavior but it should able to withstand under various condition. Probably the biomass from microbial origin has a special interest towards biosorption. There are number of biomaterials available but they should satisfy the need of the process

with high metal uptake. The AlgaSORB[TM] and AMT – Bioclaim[TM] are well known commercial branded biosorbents produced from algal sea weeds. Inadequate acquaintance on the adsorption characteristics of the above sorbents in fact hindered the further improvement of technological application and the process performance. Due to the insight approaches, the mechanism behind the biosorption is revealed [39], and particularly, the algal and fungal biosorption mechanism is intensively undertaken [40]. The study report shows that sulphate gets bound to the sulpahte moieties which act as the binding site for the metals [7]. The brown algae are enriched with alginates. It contains 20 – 40% of the dry weight of cells and some sulfated polysaccharides are moulded in the cell wall. The functional groups present in the form of carboxyl group of alginates are the underlying root for the metal binding [41].

Table.3 Main binding groups in brown algae

Binding chemical group	Lig and Atom	Biopolymer
Carboxyl	Oxygen	Alginic acid
Thiol	Sulfur	Amino acids
Sulfonate	Sulfur	Sulfate polysaccharides, fucoidan
Amine	Nitrogen	Amino acids, peptidiglycan
Amide	Nitrogen	Amino acids

7. MODIFICATION OF BIOMASS FOR AN ENHANCED SORPTION

The surface of the biomass acts as a platform for the biosorption. As the biosorption process principally takes place on the surface of the biomass, the modification of surface significantly alter its biosorptive capacity and function [42-44]. A quite large number of chemical, physical and other modification methods have been employed to improve the biosorption capacity. The various methods for modification for better biosorbents have been listed above.
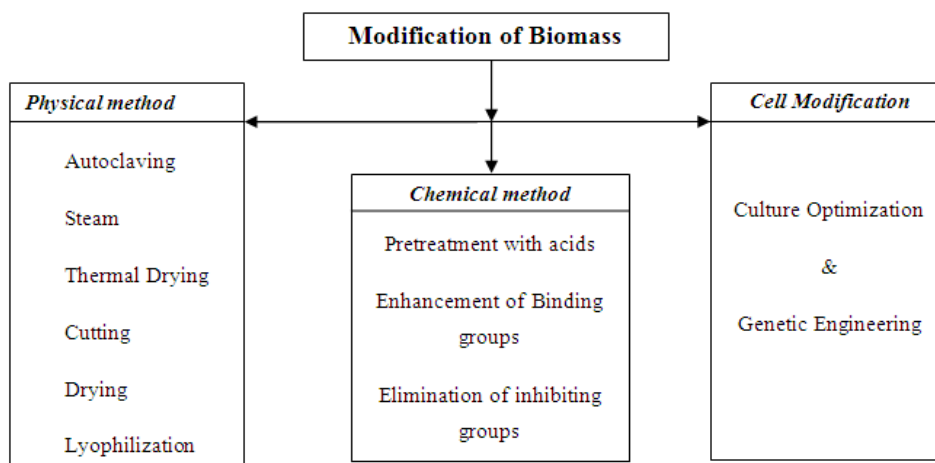

Fig.1Types of modification of biomass

Ideally, Chemical modification has been widely used because of its simplicity and high efficiency in contrast to that of physical modification [42]. Physical modification is very simple and inexpensive, but it has poor performance compared to that of chemical modification. In depth study shows that, acid-washing perhaps can enhance the capacity of biosorbents for cationic and anionic metals or acid and basic dyes. This process mainly happens by changing the polarity of the biosorbent. Even then, some of the chemicals have a serious problem in the cell surface of the biomass. The biomass can be modified by any one of the following methods: Physical, Chemical and cell modification methods. An outline of various modification of biomass is shown in Fig.1

8. IMMOBILIZATION OF ALGAL BIOMASS

There are many problems in using raw biomass in the biosorption process basically biomass is very small in size with low density, less mechanical strength and modest rigidity. Thus, it is very difficult to withstand the high pressure operation. So, when the biomass is immobilized it would have a better shelf-life, offers an excellent handling and easily biodegradable in contrast to free biomass [45]. Therefore, it is always recommended to use the immobilized biosorbents before the sorption process. There various techniques for the immobilizing the biomaterials such as

(i) Immobilization onto inert support e.g., Immobilization of Enterobacter aerogens biofilm onto activated carbon [46-47].
(ii) Entrapment of biomass e.g., polymers like calcium alginate [48, 49], polyacrylamide [50-52] polysulfone [53], and polyethylenimine [54] were used for the immobilization.
(iii) Covalent bonding of vector compounds [55, 56].
(iv) Cross–linking of cells [55]. Covalent bonding and cross linking are the two techniques are frequently adopted in the immobilization of algal biomass.

The immobilization of Sargassum biomass with resin with amino groups cross linked with glutaraldeyde was tested for the performance of the cadmium uptake. The study report shows that the immobilized biomass shown to have higher uptake [57]. The silica gel is mainly used for algal immobilization and is considered as a common vector compound (carrier). Formaldehide, glutaric dialdehyde, divinylsulfone, formaldehyde-urea mixtures are other matrix used for algal biomass immobilization [55].

9. DESORPTION AND REGENERATION

The biomass can be reused by the process of desorption where metal adsorbed biomass is treated with alkaline solutions such as EDTA, NaOH or $CaCl_2$ [58-61], mineral acids such as: HCl, HNO_3, H_2SO_4 [59, 62, 63] or organic compounds such as formaldehyde and tiourea [58], [62] or distilled water [33] can be used as eluant of adsorbed metals. It is noted that the brown algae which has a thick thallus (Ex: Sargassum sp) can be used for many cycles compared to that of green algae (Ulva Sp) due to the thin thallus.

In 2002, Jalali and his coworkers eluted 95% of lead from Sargassum biomass by treating with 0.1M HNO_3 for 15 min [59]. The same biomass was reused for ten cycles of sorption-desorption processwithout any significant damage to the biomass. Overall the lead uptake remained constant of 98% [59]. Zeroual et al. (2003) found that the protonated biomass had a better adsorption compared to that of raw biomass. The binding sites present in the biomass are made vacant by the elimination of impurities and other metals [63].

10. COMMERCIAL ALGAL BIOSORBENTS

Based on the critical analysis of various microbial biomass a few potent metal sequestering biosorbents have been commercialized. AlgaSorb[TM] a potent algal biosorbent is a potent bisorbent developed from fresh water alga, Chlorella vulgaris to treat the metal bearing wastewater [64]. AlgaSorb[TM] have tendency to remove the metal ions from waste water of concentration ranging from 1- 100 mg/l. It can reduce the concentration to 1 mg/l or even below can efficiently remove metallic ions from dilute solutions, i.e. 1–100 mg/l and reduces the concentration of metal(s) down to 1 mg/l or even below. The other different algal biosorbents used for the metal removal are presented in Table.4

AMT-BIOCLAIMTM (MRA) is another variant of commercial biosorbent prepared from Bacillus biomass in the form of granulated material for the recovery of metals [65]. This can be used for the treatment of cationic metals and can reduce the 99% of the metal concentration level. Particularly it is not a selective biosorbent but it can be reused by using various desorbing agents like H_2SO_4, NaOH.Bio-Fix biosorbent is produced by the mixure of one or two biomasss such as cyanobacterium (Spirulina), yeast, algae and plants (Lemna sp. and Sphagnum sp.) [65], [66, 67].Xanthum and guar gums are used to blend the biomass to give a consistent product with high stability.

11. BIOSORPTION MODELS AND ISOTHERMS

The adsorption isotherm is the basic criteria for the prediction of adsorption capacity of the sorbent [81]. All batch experiments are done with well defined systems of single metal and varying the parameter such as pH, metal concentration, temperature, biomass dosage etc. The batch adsorption experiment is conducted by contacting the metal solution with a quantified biosorbent for a particular interval of time when the equilibrium is reached. The sorbate uptake is calculated as follows

$$Q = \frac{V(C_i - C_f)}{M} \qquad (1)$$

Where, Q is sorbate uptake (mg/g) V is the volume of the solution (L); C_i and C are initial and final concentrations of the sorbate (mg L^{-1}); M is mass of the sorbent (g).

Adsorption isotherm curves help to compare the sorbate uptake capacity of the sorbent. Mechanistic or empirical equations are used to model the effect of isothermal studies. The experimental behavior can be predicted by mechanistic model whereas the empirical equations,

Table.4 Comparison of adsorption capacity of seaweeds for metal

Biosorbent (Sea weed)	Color	Adsorbate	Q (mg/g)	pH	Temp.	Kinetic Model	Isotherm	Ref.
Turbinaria conoides	Brown	Lead	439.40	4.5	30^0C	-	Langmuir	[68]
Turbinaria ornata	Brown	Copper	147.06	6.0	-	-	Langmuir	[69]
Sargassum wightii	Brown	Copper (II)	115.00	4.5	-	-	Langmuir	[70]
Sargassum Polcysstum	Brown	Total Chromium	69.4	2.0		Pseudo 2nd order	-	[71]
Ulva reticulate	Green	Zinc (II)	135.5	5.5	30^0C	Pseudo 2nd order	Langmuir	[72]
Sargassum sp.	Brown	Cadmium	0.90 mmol/g	4.5	-	-	-	[73]
Ulva reticulate	Green	Copper (II)	74.63	5.5	-	-	Freundlich	[74]
Fucus vesiculosus	olive-brown	Copper (II)	1.85 mmol g^{-1}	-	-	-	Langmuir	[75]
Sargassum myriocystum	Brown	Lead	179.5	5.0	25^0C	-	-	[76]
Pithophora varia	Green	Chromium(III)	60.6	5.0	20.0	-	Langmuir	[77]
Sargassum wightii	Brown	Nickel (II)	18.58	4.0	-	-	-	[78]
Sargassum wightii	Brown	Cobalt (II)	20.63	4.5	-	-	-	[78]
Gracilaria	Red	Selenium	2.72	-	-	-	-	[79]
Kappaphycus alvarezii	Red	Cadmium (II)	6.06	4.0	-	-	Langmuir and Freundlich	[80]

reveals the experimental curves not the mechanism [42]. In empirical modeling 2, 3, or even 4 parameters are evaluated. By default, Langmuir and Freundlich models have been most commonly used, because of its high success rate. Experimental data can even fit well with two-parameter models.

11.1 Equilibrium isotherm models
Modeling of isotherm data is important for predicting and comparing the performance of the biosorption. There are four different models for modeling the biosorption data such as two, three and also four parameter isotherm models [70, 82]. In this review three parameter isotherm models have discussed which include Langmuir, Freundlich and Redlich – Peterson isotherm expressions. The Langmuir, Freundlich and Redlich – Peterson isotherm models are represented by the following equations [83-85] respectively,

$$Q = \frac{Q_{max}bC_f}{1+bC_f} \qquad (2)$$

$$Q = K_F C_f^{1/n} \qquad (3)$$

$$Q = \frac{K_{RP}C_f}{1+a_{RP}C_f^{\beta_{Rp}}} \qquad (4)$$

where Qmax is the maximum metal uptake (mg/g), b is the

Langmuir equilibrium constant (L/mg), K_F is the Freundlich constant (L/g), 1/n, n is the Freundlich constant, K_{RP} is the Redlich–Peterson isotherm constant (L/g), a_{RP} is the Redlich–Peterson isotherm constant (L/mg)$^\beta_{RP}$, and β_{RP} is the Redlich–Peterson model exponent.

12. BIOSORPTION KINETICS

In addition to the biosorption isothermal models, thermodynamic and kinetic models are used to explain the performance and mechanism of the biosorption process. For the pilot scale of operation, the kinetic performance of the adsorbent has a great impact. The residence time required for the complete biosorption process, solute uptake rate is predicted from the kinetic analysis. So the adsorption kinetics is very important for the effective determination of adsorbent [86-95] on the other hand, there are several problems exist in the scale up of the biosorption. The following three steps are essential for the development of the adsorption models [96]: (1) The film diffusion occurs i.e the adsorbent is surrounded by the liquid film (2) Internal diffusion or intra-particle diffusion is said to occur where the diffusion of the liquid from the pores of adsorbent and (3) mass action i.e in the adsorbate and the active sites, the adsorption or desorption takes place.

Several researchers have given different opinions on adsorption kinetics which have been reviewed meticulously for the batch biosorption studies. Hence it would significantly assist the current researchers to select a suitable biosorbent for the large scale operation. This review mainly aimed to improve the modern adsorption kinetic modeling. Therefore some commonly used batch adsorption kinetics was critically reviewed by giving more importance to the boundary conditions.

12.1 Pseudo-first-order rate equation

Lagergren(1898) investigated the adsorption of oxalic acid and malonic acid onto the charcoal [97]. In order elucidate to the rate of the solid – liquid adsorption process a first order rate was applied to describe the adsorption rate based on adsorption capacity equation which is alleged to be the first kinetic model. It is written as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (5)$$

where q_e and q_t(mg/g) are the adsorption capacities at equilibrium and time t (min), respectively. K_1 (min^{-1}) is the pseudo-first-order rate constant for the kinetic model. Integrating Eq. (4) with the boundary conditions of q_t=0 at t=0 and q_t=q_t at t=t, yields [98]:

$$ln\left(\frac{q_e}{q_e - q_t}\right) = K_1 t \qquad (6)$$

Eq (5) can be rearranged as:

$$log(q_e - q_t) = log\, q_e - \frac{k_1}{2.303}t \qquad (7)$$

Lagergren's first order rate equation has been called pseudo-first-order, in order to differentiate the kinetic equation based on the capacity of different adsorbent from various solution concentrations [99]

Pseudo first order rate equation has a wide application in the depiction of adsorption property of various pollutants from wastewater say for example, adsorption of methylene blue and malachite green from aqueous solution by broad bean peels and oil palm trunk fibre respectively [100,101].

12.2 Pseudo-second-order rate equation

In 1995, Ho demonstrated the biosorption kinetics of peat for the adsorption of divalent metal ions onto peat [102]. In this type of metal sorption normally the biosorption takes place by cation- exchange process. Principally, in the biosorption of metals there is tight bond formation between the divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity of the peat. Therefore, the peat-metal reaction may be presented as shown in below equations, which can be dominant in the adsorption of Cu2$^+$ ions onto peat [103]:

$$2P^- + Cu^{2+} = CuP_2$$
$$2HP + Cu^{2+} = CuP_2 + 2H^+$$
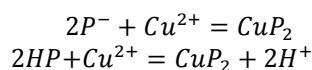
where P^- and HP are active sites on the peat surface.

The above two equation is developed based on the assumptions such as adsorption may be second order and rate is limited by the valence forces between the peat and divalent metal ions by covalent bond formation. Also it is assumed that Langmuir adsorption isotherm is said to be followed [104].

The study shows that rate of adsorption dependent on the divalent metal ions. Hence in the equations at definite time't' and at equilibrium the adsorption is dependent upon the divalent metal ions. Thus in the peat and metal sorption reaction presented above, the Cu^{2+} ions can be dominant on the peat [103] where the active sites on the peat surface are P^- and HP.

The typical second-order rate equation in solution systems is [105]

$$\frac{dC_t}{dt} = -K_2 C_t^2 \qquad (8)$$

Eq. (8) was integrated with the boundary conditions of C_t=0 at t=0 and C_t=C_t at t=t to yield

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_0} \qquad (9)$$

where C_0 and Ct (mg/L) is the concentration of solute at equilibrium and at time t (min), respectively, and k_2 (L/(mg·min)) is the rate constant. In earlier years, the second-order rate equations were reasonably applied to describe adsorption reactions occurring in soil and soil minerals. Recently, the equation has also been used to describe fluoride adsorption onto acid-treated spent bleaching earth [106] and phosphamidon adsorption on antimony (V) phosphate cation exchanger [107].

12.3 Kinetic Analysis

A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [99], [102]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (10)$$

where k_1 is the rate constant of pseudo-first-order adsorption and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, equation (9) becomes

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form [99, 102]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (11)$$

where k_2 is the rate constant of pseudo-second-order adsorption. Integrating equation (11) and applying the initial conditions, we have

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (12)$$

or equivalently,

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

12.4 Test of kinetic models

The values of q_e used to fit the pseudo-first-order equation are taken from previous studies [108]. In order to quantitatively compare the applicability of each model, a normalized standard deviation D_q is calculated

$$\Delta q\% = 100X \sqrt{\frac{\Sigma[(q_{t,exp}-q_{t,Cal})/q_{t,exp}]^2}{(n-1)}} \qquad (14)$$

13. ADSORPTION DIFFUSION MODELS

Generally film diffusion, intra-particle diffusion and mass action are involved in a typical solid-liquid adsorption. The kinetic study can be mainly applied for the adsorption process where the liquid film diffusion or intra-particle diffusion either any of the one rate limiting step is to be occurred but in the case of physical adsorption the mass action is very fast and quick so the kinetic study is negligible [109]. Hence the diffusion models are mainly aimed to describe the film diffusion and/or intra-particle diffusion.

13.1 Liquid film diffusion model
13.1a. linear driving force rate law
According to the mass balance law the accumulation of solute in the solid phase is equal to the solute transferred across the liquid film. The rate of solute accumulation in a solid particle is $V_P\left(\frac{\partial \overline{q}}{\partial t}\right)$,
where $\overline{q}$ represents the average solute concentration in the solid, and V_p the volume of the particle. Meanwhile the rate of solute transfer across the liquid film is proportional to the surface area of the particle A_s and the concentration driving force $(C-C_i)$. Therefore, it equals to $k_f A_s (C-C_i)$, where k_f represents the film mass transfer coefficient [110]. Thus we obtain,

$$V_p\left(\frac{\partial \overline{q}}{\partial t}\right) = K_f A_s(C - C_i) \qquad (15)$$

where C_i and C denote the concentration of solute at the particle/liquid interface and in the bulk of the liquid far from the surface, respectively. Eq. (15), thus, can be rearranged to

$$\frac{\overline{\partial q}}{\partial t} = K_f \frac{A_s}{V_p}(C_s - C_i) \qquad (16)$$

The ratio As/Vp that is the particle surface area per unit particle volume can be defined as S_0. Then, Eq. (16) can be written as

$$\frac{\overline{\partial q}}{\partial t} = K_f S_0(C - C_i) \qquad (17)$$

Eq.(16) is called as "linear driving force" rate law, which is generally practically used to depict the mass transfer through the liquid film.
13.1b Film diffusion mass transfer rate equation
The film diffusion mass transfer rate equation presented by Boyd et al., (1947) is

$$ln\left(1 - \frac{q_t}{q_e}\right) = -R^l t \qquad (18)$$

$$R^l = \frac{3D_e^l}{r_0 \Delta r_0 K^l} \qquad (19)$$

where $R^l (min^{-1})$ is liquid film diffusion constant, De^l (cm^2/min) is effective liquid film diffusion coefficient, r_0 (cm) is radius of adsorbent beads, Δr_0 (cm) is the thickness of liquid film, and k' is equilibrium constant of adsorption.

A plot of $ln(1-q_t/q_e)\sim t$ should be a straight line with a slope $-R^l$ if the film diffusion is the rate limiting step. Then the corrected liquid film diffusion coefficient De^l can be evaluated according to Eq. (18). Several liquid/solid adsorption processes follows the film diffusion mass transfer.
The film diffusion mass transfer rate equation has been successfully applied to model several liquid/solid adsorption cases, e.g., NDA-100 a polymeric adsorbent used for the adsorption of phenol by under different temperature and initial concentration conditions [109].

13.2 Intra particle diffusion model

13.2a Homogeneous solid diffusion model (HSDM)

The mass transfer in a amorphous and homogeneous sphere can be evidently described using a typical intra particle diffusion model so-called as homogeneous solid diffusion model (HSDM) [110]. The HSDM equation can be constructed as

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \qquad (20)$$

where D_s is intra particle diffusion coefficient, r radial position, and q the adsorption quantity of solute in the solid varying with radial position at time t. Crank (1956) gave an exact solution to Eq.(18) for the "infinite bath" case where the sphere is initially free of solute and the concentration of the solute at the surface remains constant [111]. External film resistance can be neglected according to the constant surface concentration [110]. Subsequently, Crank's solution is written as follows

$$\frac{q}{q_s} = 1 + \frac{2R}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}sin\frac{n\pi r}{R}exp\left(\frac{-D_s n^2 \pi^2 t}{R^2}\right) \quad (21)$$

where R is the total particle radius.
The average value of q in a spherical particle at any particular time, defined as $\overline{q}$, is presented as follows:

$$\overline{q} = \frac{3}{R^3}\int_0^R q(r)r^2 dr \qquad (22)$$

where q(r) is the local value of the solid-phase concentration. By substituting for q(r) in Eq.(22), we get the following equation:

$$\frac{\overline{q}}{q_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp\left(\frac{-D_s n^2 \pi^2 t}{R^2}\right) \qquad (23)$$

where q_∞ denotes at infinite time the average solute concentration in the solid phase
For a short interval of time, when $\frac{\overline{q}}{q_\infty} < 0.3$ Eq. (23) can be simplified as

$$\frac{\overline{q}}{q_\infty} = 6\left(\frac{D_s}{R_2\pi}\right)^{1/2} t^{1/2} \qquad (24)$$

By plotting $\overline{q}/q_\infty$ against $t^{1/2}$ the value of Ds from short-time data can be determined. From Eq. (24) it is concluded that the rate of adsorption decreases as the particle size increases and vice versa
Eq. (23) can be written as follows to get the solution for a long time,

$$\frac{\bar{q}}{q_\infty} = 1 - \frac{6}{\pi^2} exp\left(\frac{-D_s\pi^2 t}{R^2}\right) \qquad (25)$$

Eq. (25) is linearized and written as follows

$$\ln\left(1 - \frac{\bar{q}}{q_\infty}\right) = \frac{-D_s\pi^2}{R^2}t + \ln\frac{6}{\pi^2} \qquad (26)$$

Similarly, the value of D_s from long-time data can be determined by plotting of

$$\ln\left(1 - \bar{q}/q_\infty\right) \text{ vs t.}$$

However, HSDM is not valid for a long time. Therefore, the equation is somewhat valid for the short time [110]. Currently, HSDM has been applied for the adsorption organic acids such as salicylic acid and 5-sulfosalicylic acid from aqueous solutions by the hyper cross-linked polymeric adsorbent NDA-99 and NDA-101.

The diffusion coefficient D_s obtained from then adsorption system of pentachlorophenol (PCP) onto activated carbon from the batch kinetic adsorption experiments is applied for the prediction of adsorption breakthrough curves in fixed column and also used to design a suitable packed bed column for the PCP removal [112].

13.2 b Weber-Morris model

Weber-Morris found that rather than the contact time t, solute uptake varies almost proportionally with $t^{1/2}$ in many of the adsorption processes [113]

$$q_t = k_{int}t^{1/2} \qquad (27)$$

where k_{int} is the intraparticle diffusion rate constant. According to Eq.(19), at intra-particle diffusion is a rate-limiting step a plot of q_t against $t^{1/2}$ should be a straight line with a slope k_{int}. Particularly, in the case of Weber-Morris model the $q_t \sim t^{1/2}$ plot should go through the origin if the rate limiting step is intra-particle diffusion. When the slope is not equal to zero obviously the adsorption kinetics is controlled neither by diffusion nor intra-particle diffusion.

13.3 c Dumwald-Wagner model

Dumwald-Wagner proposed a different intraparticle diffusion model as [114]

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2 Kt\right) \quad (28)$$

where K (min^{-1}) is the rate constant of adsorption.

A simplified Dumwald-Wagner model is obtained from Eq. (28) as,

$$\log(1 - F^2) = -\frac{-K}{2.303}t \qquad (29)$$

A plot of $\log(1 - F^2)$ Vs t should be linear and the rate constant K can be obtained from the slope.

Hence, Dumwald-Wagner model has shown to be reasonable to model different kinds of adsorption systems, e.g., Adsorption of p-toluidine onto cross linked polymeric adsorbents from aqueous solutions.

14. CONCLUSION AND PERCEPTION

In the present review, the adsorption capacity of various supernatural marine algae is reviewed meticulously. From the literature it is concluded that seaweeds has an excellent potential for the adsorption of heavy metals from the aqueous solution. The ubiquitous nature of seaweeds makes the waste water treatment much simpler. The impressive Brown marine algae have a propensity particularly to sequester heavy metals. Through this review paper we would like to tell that seaweeds would be one of the main biosorbent for the recovery of heavy metals. Globally, there is wide range of biomaterials available even then sea weeds have their own significance because of the cost effective biological material with high adsorption efficiency. This review has given a nut shell about the significance of the sea weeds and their adsorption behavior. Seaweeds are fast growing and abundant source in some cases they threaten the tourist people by fouling beaches and spoiling the environment. Of course it is an alternate way to dispose the sea weeds and benefiting the local communities. The seaweeds are available throughout the year. Reusability is an important factor while choosing an effective biosorbent. Seaweeds have an effective reusability without losing the adsorption property. This review has summarized about the various analytical techniques applied for the biosorption process. In addition we have added the different isotherm models, kinetic models for determining the adsorption capacity of seaweeds. Overall, this paper would definitely help the academicians and industrialist who are finding solution for remediating the environmental issues.

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