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BIOSORPTION: A REVIEW ON MECHANISM, ISOTHERMS AND KINETICS

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ABSTRACT

The wastewaters of many industries contain heavy metals. A variety of methods have been developed for removal of metal ions from wastewaters such as precipitation, evaporation, electroplating, ion exchange, membrane filtration, carbon adsorption, etc. A variety of waste biological materials have been used as biosorbents for the removal of heavy metal ions from waste waters. The main advantage of biosorption is that it is a cheap and efficient process. This review discuss the mechanism of metal uptake, biosorption technology, the features of biosorption, isotherms and kinetic models to characterize the suitability of biosorption of heavy metals on biosorbents.

KEYWORDS: Heavy metal pollution, Biosorption process, Isotherms, Kinetics of biosorption.

INTRODUCTION

The water pollution due to heavy metals is the major and challenging environmental problem. Direct sources include waste water from industries, refineries contaminants that enter to water supply from soils or ground water systems and from the atmosphere via rain water.[1] The treatment of heavy metals is of special concern due to their non bio-degradable and toxic nature.[2] Through food chains, they accumulate in the human body and causes serious disorders.[3] The various anthropogenic activities that introduce the heavy metals in the environment are mining and smelting of ores, municipal waste, burning of fossil fuels, industrial effluents and agricultural activities.[4-22] The conventional methods used for removal of heavy metals from polluted water are chemical precipitation, ultra filtration, ion exchange, reverse osmosis, electro winning, carbon adsorption and phytoremediation. These methods are not effective, expensive and take long time for heavy metal ion removal. The biosorption is relatively new, efficient, low cost and eco-friendly method for removal of heavy metal using waste biomass as biosorbents. The biosorption can be defined as the ability of biological material to accumulate heavy metals from waste water through metabolically mediated or physicochemical pathways of uptake.[23-26]. Recent biosorption experiments have focused attention on waste materials from large scale industrial operations.[27-29]. A number of materials such as leaf mould, rice husk, groundnut husk, coconut husk and palm pressed fibers, coconut shell, coconut jute, coconut tree sawdust, cactus, olive stone cake and wool and pine needles have been used as bio-sorbent for the removal of the heavy metal ions.[30-37] The mechanism of biosorption is depending on the nature of biomass, types of biomaterials, properties and the chemistry of metallic solutions. The environmental conditions may affect the mechanism of biosorption.[12] The biosorption mechanism is of two types, metabolism dependent and metabolism independent.[38] Transport of metals across the cell membrane dependent on the metabolism of cell and such type of mechanism takes place only in living cells. The non metabolism dependent mechanism depends on the interaction of metals by certain functional groups present on the surface of bio-sorbents. The interaction is based on physical adsorption, ion exchange and chemical sorption. Such phenomenon does not depend on the metabolism of the cells. The metal binding groups on bio-sorbents may be polysaccharides, proteins and lipids. These components have the constituents such as carboxyl, sulphate, phosphate and amino groups. The non metabolism based mechanism is more rapid than metabolism based mechanism and can be reversible.[39, 40]

BIOSORPTION STUDY

The biosorption study have been carried out in the analytical and environmental laboratories, can be divided into four categories such as synthetic waste water, batch operation, biosorption isotherms and kinetics of biosorption.

Synthetic Waste Water

In brief, the natural waste water contains both organic as well as inorganic pollutants. This composition makes the waste water heterogeneous in nature. To set ideal conditions for a treatment of a particular pollutant becomes difficult. To overcome this problem and to have homogeneity in waste water for bench scale experiments, the synthetic waste water containing pollutants of interest is commonly used. Examples are artificial septic tanks[41], synthetic textile waste water [42], synthetic microbial waste water [43], synthetic metallic waste water[44] and synthetic dyeing waste water [45]. An industrial effluent mainly adds heavy metal ions to the water bodies. This effluent is used as an experimental solution to study the removal efficiencies of the adsorbents. In the recent past instead of using industrial effluent synthetic waste water is in practice as an experimental solution. It is the solution of some dissolved sulphate and nitrate salts and used in the bench scale experiments and more homogenous than industrial waste water samples.

Batch operation

The biosorption study is commonly carried out by batch operation. A solution containing desired concentration of metal ions was treated with a certain amount of adsorbent in a conical flask at a constant shake.[46-48] The solution was then filtered and biosorbent filtered out. The concentration of metal ions before and after adsorption is determined. Atomic absorption spectroscopy and Inductively coupled plasma are used for the determination of metal concentration in aqueous solutions, UV-Vis spectrophotometer is for determination of metal concentration in aqueous phase by measuring its color intensity, infrared absorption spectroscopy or Fourier transformed infrared spectroscopy are used for the determination of active sites present on the biosorbent, scanning electron microscopy is for the visual confirmation of surface morphology and X-ray diffraction analysis, for crystallographic structure and chemical composition of metal bound on the biosorbent. The nuclear magnetic resonance spectroscopy is used to determine the presence of active sites of the biosorbent [49,50]. The Removal efficiency of metal ions was calculated by using following equation:-

$$\textbf{Removal efficiency} = C_o - C_e / C_o * 100$$

Where C_o and C_e are the metal ion concentrations in mg/L initially and at a given time t respectively. The different process conditions have been applied for batch operation such as contact time, amount of adsorbent, pH, initial metal ion concentrations and temperature.

Biosorption isotherms

The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and solid phase when the adsorption process reaches the equilibrium state. Adsorption isotherm is basically important to describe how solutes interact with adsorbents and critical optimization of the use of adsorbents [51,52].

Langmuir isotherm model

Langmuir isotherm.[53] assumes monolayer adsorption onto a surface containing finite number adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm model is given by the following equation.

$$C_e/q_{max} = 1/K_1 b + 1/K_1 C_e$$

Where, q_{max} is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) and C_e is the metal ion concentration at given time t. K_1 and b are related with adsorption capacity and rate of adsorption. When C_e/q_{max} is plotted against C_e, a straight line with slop $1/K_1$ and intercepts $1/K_1b$ is obtained. The essential characteristic of Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter (R_L) which is defined as:

$$R_L = 1/1+b\ C_o$$

Where b is the Langmuir constant and C_o is the initial concentration of metal ions (mg/L). The value of R_L indicates that the type of isotherm model is either favorable ($0<RL<1$), unfavorable ($R_L>1$), linear ($R_L=1$) or irreversible ($R_L=0$).

Freundlich isotherm model

Freundlich isotherm [54,55] is an empirical expression based on biosorption on a heterogenous surface. The linear form of Freundlich equation is given by the following expression:

$$\log q_{max} = \log K_2 + 1/n \log C_e$$

Where q_{max} is the amount of metal ions adsorbed at equilibrium (mg/g), and C_e represents the equilibrium concentration of adsorbate (mg/L). K_2 and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. The value of K_2 and 1/n were obtained from the slop and intercept of the plot, log q_{max} versus log C_e.

Temkin isotherm model

Temkin isotherm model considers the effect of indirect adsorbate - adsorbate interaction. This interaction explains that the heat of adsorption of all the components on the adsorbent surface would decrease linearly with coverage[56,57]. The Temkin isotherm model is given by the following equation [57]

$$q_{max} = a + b \ln C_e$$

Where C_e is the equilibrium concentration of metal ions in mg/L, qe is the amount of adsorbate in mg/g, a and b are constants related to adsorption capacity and intensity of adsorption. When q_{max} is plotted against ln C_e then a and b are obtained from intercept and slope.

Kinetics of biosorption

In biosorption study, four common kinetic model are used as proposed in the literature for the determination of different kinetic models.

Pseudo – First order model

Lagergren [58] considered the expression for general form of pseudo first order kinetic model as-

$$dq / dt = k (q – q')$$

Where q and q' are the amount of metal ion adsorbate at equilibrium and at time in mg/g respectively while k is the first order rate constant in min^{-1}. By integrating this expression between the limits t = 0, q = 0 and t = t, q' = q', the following equation is obtained:

$$\log(q – q'/ q) = - k /2.303^{* t}$$

By plotting the value of log (q – q') / q) versus t, the value of the rate constant k can be obtained from the slope.

Pseudo-Second Order Model

The pseudo second order kinetic.[59] model for biosorption kinetics is given as below:

$$dq'/ dt = k (q – q')^2$$

Where k' is the second order rate constant in g/mol/min and q and q' are the amount of metal ion adsorbate at equilibrium and at time t in mg/g respectively. By integrating this equation between the limits t = 0, q' = 0 and t = t, q' = q', the following equation is obtained:

$$t / q' = 1/h + 1/q *t$$

Where $h = k \cdot q^2$ is the initial sorption rate, in mg/g·min. By plotting t/q' versus t, the values of q and k can be obtained from the slope and the intercept, respectively.

Elovich Model

The Elovich [60] kinetic model explains the chemisorptions kinetics of metal adsorbate on the adsorbent and their activation energies. Elovich equation also describes second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation cannot explain any definite mechanism for adsorbate–adsorbent interaction. This is mathematically expressed by following equation:

$$q' = a + b \ln t$$

Where a and b are the initial adsorption rate (mg/g/min) and desorption constant. These are obtained from the intercept and slop of the plot q' versus ln t.

Intra particle diffusion

Intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [61] and it controls the batch process for most of the contact time. The initial rate of intra-particle diffusion can be obtained by linearization of the curve according to equation.

$$q' = k_d t^{1/2 +} I$$

Where k_d and I are intra particle diffusion and obtained from slop and intercept of the plot q' vs $t^{1/2}$.

CONCLUSIONS:

The paper represents a review of literature on various aspects of biosorption. An attempt has been made to cover valuable literature on heavy metal removal, mechanism of biosorption, batch operation, instrumentation, isotherms and kinetic models of biosorption. There is a variety of waste biomass available in the World and this work can initiate to select waste material for the removal of heavy metal ions. Research is still in progress as different areas related to biosorption are being explored.

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