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Progress in batch biosorption of heavy metals onto algae

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ABSTRACT

Biosorption is a promising technology which pays attention to fabricate novel, cheap (low-cost) and highly-effective materials to apply in wastewater purification technology. Algae belong to a multi applicable group, which can contribute to important sectors. Their major use is to produce a wide range of primary and secondary metabolites, which applied to food, pharmaceutical and cosmetic industries. Moreover, algae have been suggested as potential feedstock for bioenergy and biofuel production. This review article collects information from published works of the last two years (2014 and 2015), discussing about the alternative use of different algae (micro and macro) in raw or modified form as promising biosorbents for water or wastewater decontamination. Some important adsorption paths were criticized as the stage of (i) equilibrium (isotherms), (ii) kinetic, and (iii) desorption. For this purpose, many factors which influence the adsorption process, such as the effect of solution pH, contact time, temperature and adsorbent's dose, were also discussed.

1. Introduction

The increase of industrial activities led to the production of toxic pollutants (in various amounts) such as heavy metals, dyes, pesticides, phenols, organic compounds, etc. [1]. Heavy metals are recognized as one of the most toxic groups which reach in food chain through the disposal of wastes to water receptors or land. Heavy metals are taxed in causing toxic effects, cancer and diseases because they cannot be degraded, [2,3].

Various methods such as adsorption, coagulation, advanced oxidation, and membrane separation have been used for the removal of heavy metals from wastewaters. However, adsorption is one of the most effective processes of advanced wastewater treatment [4]. Numerous works have been recently published with primary goal the investigation of removal of different pollutants (either in gas or liquid medium) using adsorbent materials [5–20]. Some of the widely used adsorbents materials especially for heavy metals removals from aqueous solutions are chitosans [21], nanoadsorbents [22], barks [23], wastes from olive oil industry [24], coconut based materials [25], agricultural peels [26,27], zeolites [28], clay soils [29] and betonites and vermiculites [3]. In this study, the use of algae for heavy metal biosorption is discussed.

Algae consist of two different types namely micro- and macro-algae. Macro-algae or "seaweeds" are multi-cellular plants growing in salt or fresh water. Macro-algae are generally fast growing and able to reach up to 60 m (length). According to their pigmentation, they are divided into three broad groups: (i) brown, (ii) red, and (iii) green seaweed [30,31]. Micro-algae are photosynthetic unicellar microorganisms that grow (or exist) in salt or fresh water. There are many characteristics which affect the classification of micro-algae such as, pigmentation, arrangements of photosynthetic membranes or other morphological features. At present, micro-algae are classified to four groups: (i) diatoms, (ii) green algae, (iii) golden algae and (iv) cyanobacteria (blue-green algae) [31,32].

Generally micro- and macro-algae are being studied for its multi-functional utilizations such as food, cosmetics, medicine, energy, etc. (Fig. 1) [33–36]. Moreover, algae have received a great deal of attention for decontamination of water by biosorption process. Algal biomass can be used for live or dead form in a biosorption system. Non-living biomass is more practical and favorable due to the fact that living biomass cells needs minimum nutrients and environmental conditions, while dead biomass does not. Moreover, dead biomass is not affected by the toxicity of metal ions, while they can undergo different chemical and physical pretreatments to increase their adsorption capacity.

Based on a statistical review on biosorption, algae have been used as biosorbent material 15.3% more than other kinds of biomass and 84.6% more than fungi and bacteria [37,38]. Their ability focused on the composition of cell wall which includes chitin, lipids, polysaccharides and proteins. These macromolecules contribute different functional groups such as carboxyl, hydroxyl, carbonyl, phenolic, etc., which can form coordination complexes with heavy metals. Considering their availability and low-cost, the rapid biosorption capability, high efficiency, reusability, high selectivity, no toxic waste generation, algae could be ideal and

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Nomenclature

BET	Brunauer–Emmett–Teller
D–R	Dubinin–Radushkevich isotherm equation
ELV	Elovich kinetic equation
F	Freundlich isotherm equation
FP	Fractional power
F–S	Fritz–Schlunder isotherm equation
L	Langmuir isotherm equation
L–F	Langmuir–Freundlich isotherm equation
PS1	Pseudo-first order kinetic equation
PS2	Pseudo-second order kinetic equation
R–P	Redlich–Peterson isotherm equation
S	Sips isotherm equation
T	Temkin isotherm equation

promising biosorbents. Algae can be considered as low-cost biosorbent materials, because no special treatment is needed (apart from acid or base modification). Herrera et al. found that an approximate cost of biosorption 10 g of Ag(II) onto cellulose phosphate was about 2$ USD [39]. Additionally, low-cost biosorption process using algae as adsorbent has lately been introduced as an alternative (unit cost of virgin algae is approximately ranging from 1$ USD to 3/kg) [40].

The composition of the cell wall of algae plays a significant role in the biosorption process [31]. The cell wall of algae consists of different components such as polysaccharides, proteins and lipids. Moreover it contains a number of many functional groups, which also play a key role in the biosorption of metals from aqueous solutions. Regarding macroalgae, brown algae cell walls are composed mainly from cellulose, alginic acid, polymers complexed with light metals such as sodium, potassium, magnesium, calcium, and polysaccharides. The predominant active groups are alginates and sulfate [41]. Green algae have mainly cellulose, while high percentage of the cell wall is protein bonded to polysaccharides. Proteins contain functional groups such as amino, carboxyl, sulfate, and hydroxyl, which participate significantly to biosorption process [42]. Red algae contain cellulose in cell wall, but their biosorption capacities can be mainly attributed to the presence of sulfated polysaccharides made of galactans [41].

Micro-algal cell wall consisted mainly of polysaccharides, proteins, and lipids, which offer several functional groups (i.e., –COOH, –OH, $–PO_3$, $–NH_2$, –SH). The latter confers a net overall negative charge to the cell surface, and concomitantly a high binding affinity for metal cations via counterion interactions. The cell walls of micro-algae constitute proteins, which are made up of amino acids, that provide groups (i.e., $–NH_2$), facilitating metal binding [43]. Additionally, the polysaccharides of the cell wall also provide amino and carboxyl groups, as well as sulfate ones. Chojnacka et al. confirmed the latter by stating that algal cell wall components such as peptidoglycan, teichuronic acid, teichoic acid, polysaccharides and proteins, are polyelectrolytes carrying charged groups (such as carboxyl, phosphate, hydroxyl or amine) [44].

There are a few review articles focused on the use of algae for removal of heavy metal ions from water media [31,41,45]. To our knowledge, there is a lack of updated application-trends for algae utilized as biosorbents. For this purpose, in this review article, fabricated (raw or treated) novel algae biosorbents are summarized and discussed, but only for the very last time period (only 2014–2015). Isotherm, kinetic, and equilibrium modeling were discussed in details. Moreover parameters which affect the biosorption process, such as the effect of solution pH, contact time, temperature and biosorbent's dose are also commented.

2. Biosorption modeling

In order to develop an effective and accurate design model for the removal of pollutants from aqueous media, biosorption kinetics and equilibrium data are required.

2.1. Isotherm models

It is necessary to form the most appropriate biosorption equilibrium correlation in the attempt to discover innovative adsorbents in gain access to an ideal biosorption system [46] which is vital for consistent prediction of biosorption parameters and quantitative comparison of biosorbent behavior for various biosorbent systems (or for varied experimental conditions) [47,48]. Adsorption isotherms, which is a common name of equilibrium relationships, are essential for optimization of the biosorption mechanism pathways, expression of the surface properties and capacities of biosorbents, and productive design of the biosorption systems since they explain how pollutants interrelate with the biosorbent materials [49,50].

Explaining the phenomenon through which the preservation (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a persistent temperature and pH takes places, in broad-spectrum, an adsorption isotherm is an invaluable curve [51,52]. The mathematical association which establishes a significant role towards the modeling analysis, operational design and applicable practice of the biosorption systems is normally represented by plotting a graph between solid-phase and its residual concentration [53].

When the concentration of the solute remains unchanged as a result of zero net transfer of solute biosorbed and desorbed from biosorbent surface, a condition of equilibrium is achieved. These associations between the equilibrium concentration of the adsorbate in the solid and liquid phase at persistent temperature are defined by the equilibrium biosorption isotherms. Linear, favorable, strongly favorable, irreversible and unfavorable are some of the isotherm shapes that may form.

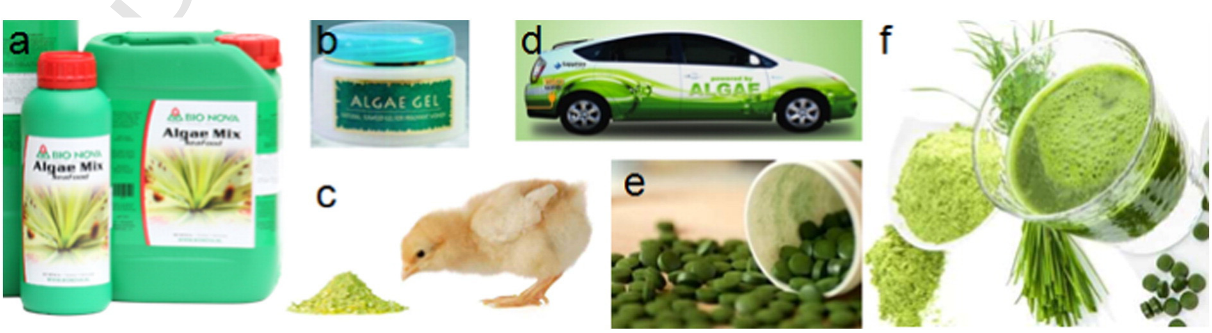

Fig. 1. General uses of algae: (a) fertilizers; (b) cosmetics; (c) animal feed; (d) biofuels; (e) medicine; (f) human food.

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