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Review

Valorisation possibilities of exhausted biosorbents loaded with metal ions – A review

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ABSTRACT

Biosorption is considered one of the most promising methods for removal of metal ions from aqueous effluents, due to its low-cost and eco-friendly characteristics. However, the exhausted biosorbents loaded with metal ions, obtained at the end of biosorption processes, are still a problem which should be solved to increase the applicability of biosorption on an industrial scale. In this study are examined three possibilities for the valorisation of exhausted biosorbents loaded with metal ions, namely: (i) regeneration and reuse of biosorbents in multiple biosorption cycles, (ii) the use of exhausted biosorbents as fertilizers for soils poor in essential microelements, and (iii) the pyrolysis of exhausted biosorbents, under well defined conditions. The main advantages and disadvantages of each valorisation possibility are reviewed in order to find the best way to use these cheap materials in accordance with the principles of the circular economy and thereby contributing to the development of sustainable biosorption technology.

1. Introduction

The large utilization of metal ions in various industrial sectors has determined the degradation of ecosystems quality, mainly due to the discharge of inadequate treated industrial wastewater, into environment (Verlicchi and Zambello, 2014; Wu et al., 2015). Therefore, an important issue from the perspective of environmental protection is still the finding of appropriate method for the removal of metal ions from aqueous effluents, which should fulfil both technological and economical requirements, in order to be applied on an industrial scale.

In present, various methods, such as chemical precipitation, electrochemical techniques, membrane related processes, osmosis, ion exchange, coagulation, etc. (Fu and Wang, 2011; Rivas and Palencia, 2011; Abdel-Aziz et al., 2013; Agwaramgbo et al., 2013), are used for the treatment of industrial effluents containing metal ions before their discharge. Unfortunately, the utilization of such methods has several important disadvantages, such as incomplete removal of metal ions, poor selectivity, high costs, high energy consumption, generation of large amounts of waste sludge, etc. (Fu and Wang, 2011; Abdel-Aziz et al., 2013), which requires certain precautions in their application on an industrial scale.

Unlike these methods, biosorption processes, involving the retention of metal ions on solid materials of biologic origin, generally called biosorbents, seems to be a viable alternative, mainly due to reduced costs, simplicity in operation and ease of adaptation on an industrial scale (Sud et al., 2008; Fu and Wang, 2011; Akunwa et al., 2014). Generally, an efficient biosorption system for metal ions removal from aqueous effluents depends mainly by the biosorptive performances of biosorbent and its preparation cost, the last requirement being directly related by the availability of the biosorbent, and the number and complexity of its preparation steps (Gupta et al., 2015). Thus, various kinds of biomasses, such as: agricultural waste, food organic waste, algae, fungi, bacteria, etc. have been tested for the removal of various metal ions from aqueous effluents, either toxic (Pb(II), Hg(II), As(III/V), Cd(II), etc.), either with low toxic potential or even essential microelements (Cu(II), Zn(II), Co(II), Ni(II), etc.) (Farooq et al., 2010; Michalak et al., 2013; Anastopoulos and Kyzas, 2015; Gupta et al., 2015; Bulgariu and Bulgariu, 2016), in order to finds a viable alternative for the cleaning of industrial wastewater before discharging it into the environment. However, several obstacles need to be overcome

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before biosorption becomes an easy-to-use method in the industrial wastewater treatment.

Thus for example, improving of biosorption capacity of biomasses used as biosorbents, by various chemical activation treatments is still a current issue in literature (Bulgariu et al., 2011; De Gisi et al., 2016; Moyo et al., 2017; Smolyakov et al., 2017). This because a high biosorption capacity of a given biomass in well defined experimental conditions, besides improving the performance of the biosorption system, determines the generation of lower amounts of exhausted biosorbent loaded with metal ions. The exhausted biosorbents loaded with metal ions, resulted after biosorption processes are also considered hazardous for the environment, since the retained metal ions can be easily released from biomass and can cause the pollution soil or water. This is why the disposal of exhausted biosorbents via landfill, after they are no longer useful, is not a viable solution (Gupta et al., 2015), from the environmental protection point of view. Therefore, the problem of exhausted biosorbents loaded with metal ions resulted after biosorption is probably the most important obstacle that limits the practical applicability of biosorption method on a large scale, and for that solutions still needs to be found.

In recent years, many studies have been focused on the potential use of exhausted biosorbents loaded with metal ions, in order to highlight the valorisation possibilities of these materials obtained after biosorption, and to transform these waste in value-added products (Chouchene et al., 2014; Dodson et al., 2015; Reddy et al., 2017). Thus, the use of exhausted biosorbents loaded with metal ions as fertilizers, feeds additives, catalysts, or for extraction of some biologically active compounds (Michalak and Chojnacka, 2009; Zhang et al., 2014; Ding et al., 2016; Liu et al., 2016; Bădescu et al., 2017; Reddy et al., 2017) represents the most important possibilities for their valorisation, according to literature studies. Unfortunately, all these valorisation possibilities have been tested only at laboratory scale and for particular exhausted biosorbents, and therefore further studies are needed before they can be widely used to solve the problem of biomass waste loaded with metal ions.

In this study, three possibilities for the valorisation of exhausted biosorbents loaded with metal ions are analyzed both from technological and environmental perspectives, in order to find the best way to minimize the problem of exhausted biosorbents resulted after biosorption. These are: (i) regeneration and reuse of biosorbents in multiple biosorption cycles, (ii) the use of exhausted biosorbents as fertilizers for soils poor in essential microelements, and (iii) the pyrolysis of exhausted biosorbents, under well defined conditions. In each case the main advantages and disadvantages are highlighted to delimit the applicability area of these valorisation possibilities of exhausted biosorbents loaded with metal ions, in line with the principles of circular economy and sustainable development.

2. Experimental evaluation of biosorption/recovery performances

The experimental methodology used for such studies generally involves two successive stages: first stage is the retention of metal ions from aqueous media onto biosorbent, in well defined experimental conditions, followed by recovery of the retained metal ions by one of the three specific methods considered in this case. In Fig. 1 are illustrated schematically the most important steps that should be included in such experimental methodologies.

It should be also mentioned that at least at laboratory scale, the chemical reagents are all of analytical grade and are used without further purification, and for the preparation of working solutions distilled water is used.

On the other hand, for the quantitative evaluation of biosorption/recovery performances, the metal ions concentration in aqueous solutions before and after biosorption/recovery processes must be determined. Most often, the atomic absorption spectrometry is used for this purpose, due to the high selectivity of this method, but also, the analysis of metal ions content by UV-VIS absorption spectrometry can be found in literature (Dean, 1995).

Based on experimentally obtained values of metal ions concentration, the evaluation of biosorption/recovery performances can be done using the following quantitative parameters:

$$\text{(a) for biosorption:} q_b = \frac{(c_0 - c)\cdot V}{m};\ R_b = \frac{c_0 - c}{c_0}\cdot 100 \tag{1}$$

$$\text{(b) for recovery:} q_r = \frac{(c - c_0)\cdot V}{m};\ R_r = \frac{c - c_0}{c}\cdot 100 \tag{2}$$

where: q_b is the amount of metal ions retained per weight unit of biosorbent; q_r is the amount of metal ions or released from weight unit of biosorbent; R_b is the removal percent; R_r is the recovery percent; c_0, c are initial and final (at equilibrium) concentration of metal ions in aqueous solution; V is volume of solution; m is the mass of biosorbent used in biosorption or desorption experiments.

3. Possibilities for the valorisation of exhausted biosorbents

As was already mentioned, in this study are examined three valorisation possibilities of exhausted biosorbents loaded with metal ions, namely:

(i) regeneration and reuse of biosorbents in multiple biosorption cycles,
(ii) use of exhausted biosorbents as fertilizers for soils poor in essential microelements,
(iii) pyrolysis of exhausted biosorbents,

to find a possible solution for the problem of exhausted biomasses, which is one of the most important obstacle in the practical use of biosorption, on a large scale.

The selection of a suitable valorisation of exhausted biosorbents loaded with metal ions depends mainly on the type of metal ions retained during of biosorption, the chemical composition of industrial wastewater treated by biosorption, and the nature of biomass material used as biosorbent. Several arguments that allow the correct choice of one of the three proposed options will be presented below.

3.1. Desorption of metal ions and regeneration of exhausted biosorbents

One of the most often proposed modality for the valorisation of exhausted biosorbents loaded with metal ions is the recovery of retained metal ions and the regeneration of biosorbents by desorption. In this way the release of retained metal ions in aqueous solution is achieved, which can be reintroduced in the industrial activities, concomitant with the regeneration of biosorbents, which can be used in other biosorption cycles.

The desorption of metal ions involves the treatment of exhausted biosorbents with a suitable desorption agent, in well selected experimental conditions (volume and concentration of desorption agent, temperature, contact time, etc.), when the retained metal ions are replaced by the other ions from desorption agent composition (Lasheen et al., 2012; Robalds et al., 2016; Kolodynska et al., 2017). The elementary processes involved in desorption of metal ions from exhausted biosorbents are typical ion exchange processes, and are schematic illustrated in Fig. 2.

According with the studies from literature (Gupta et al., 2015; De Gisi et al., 2016; Tran and Chao, 2018), various mineral acids (such as: HCl, HNO_3, etc.), inorganic salts (such as: NaCl, $CaCl_2$, $NaNO_3$, KNO_3, etc.), or complexing agents (as EDTA), in different concentrations can be used for the quantitative desorption of retained metal ions and the biosorbents regeneration. In Table 1 are summarized several examples of desorption systems used for the recovery of retained metal ions and the regeneration of biosorbents, according with some recent studies