New Biotechnology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

New Biotechnology

journal homepage: www.elsevier.com/locate/nbt

Full length article

Biosorption of lead ions from aqueous effluents by rapeseed biomass

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ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form 26 July 2016
Accepted 23 August 2016
Available online xxx

Keywords:
Biosorption
Lead
Rapeseed
Batch conditions
Fixed-bed column
Wastewater

ABSTRACT

Lead, as well as other heavy metals, is regarded as priority pollutant due to its non-biodegradability, toxicity and persistence in the environment. In this study, rapeseed biomass was used in the biosorption of Pb(II) ions in batch and dynamic conditions, as well as with tests for industrial wastewater. The influence of initial concentration (5–250 mg/L), pH and contact time (0.5–6 h) was investigated. The kinetic data modeling resulted in good correlations with the pseudo-second order and intraparticle diffusion models. The maximum sorption capacities of Pb(II) were 18.35, 21.29 and 22.7 mg/L at 4, 20 and 50°C, respectively. Thermodynamic parameters indicated the spontaneity and endothermic nature of lead biosorption on rapeseed biomass. The biosorption mechanism involves both physical and chemical interactions. The breakthrough curves at 50 and 100 mg/L were determined and evaluated under dynamic conditions. The breakthrough time lowered with increasing the influent Pb(II) concentration. The experimental data obtained from fixed-bed column tests were well fitted by Thomas and Yoon-Nelson models. The calculated sorption capacities were in good agreement with the uptake capacity of Langmuir model. The applicability of rapeseed to be used as a sorbent for Pb(II) ions from real wastewater was tested, and Pb(II) removal efficiency of 94.47% was obtained.

1. Introduction

Human activities, through industrial and agricultural processes, causes surface water quality degradation, leading to problems related to supply of drinking water or recycling of wastewater. Among the multitude of pollutants found in wastewater discharges, heavy metals generate serious environmental and health concerns. These compounds are known for their ability to migrate between environmental compartments (e.g. from sediments into water) and to accumulate in living organisms [1,2]. Heavy metals present toxic and non-biodegradable features, which is why once they reach the aquatic environment, they produce impacts on the aquatic biota, as well as to the crops near the water body, and then arrive in the human body in a more concentrated form than that of the lower food chain segments.

From the heavy metals category, lead has raised multiple concerns due to its frequent occurrence in wastewaters and its significant impacts on human health. Lead is present in effluents coming from smelters and refineries, battery manufacturing, steel industry, printing, glass manufacturing [3,4]. In humans, lead poisoning readily affects young children, causing neurodevelopmental problems even at low concentrations. Pb (II) ions present high affinity for thio (—SH), oxo (=O) and phosphate (PO_4^{3-}) groups that are found in some enzymes, and also ligands and biomolecules from the human organism and affect the membrane permeability of organs and haemoglobin synthesis [5]. Lead bioaccumulates in bones (half-time over 20 years), and affects the nervous and reproductive systems, red blood cells and kidney, and due to its enzyme inhibitor effects, is a probable carcinogenic [3,6]. Lead is listed as a priority pollutant by the US Environmental Protection Agency [7]. In drinking water, World Health Organization has set up as maximum allowable concentration for Pb(II) the limit value of 0.01 mg/L. In another classification [8], Pb is a metal of high priority for both removal and recovery from water and wastewater before discharge into the environment.

A number of processes are applied to minimize lead concentration in wastewater and they involve chemical precipitation, reduction, electrochemical methods, ion exchange, adsorption, flotation [9–13]. These methods have several disadvantages that influence their applicability, including significant capital and operational costs, addition of chemical reagents and generation of hazardous wastes, energy demand, low efficiency for diluted wastewaters [14–16]. In this context, biosorption, a subcategory of adsorption, has gain interest in recent years due to its efficiency in

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http://dx.doi.org/10.1016/j.nbt.2016.08.002
1871-6784/

mitigating heavy metals pollution of aqueous effluents, in particularly of low concentration [13].

Biosorption is based on the potential of any biological material (i.e. biomolecules or different biomass) to sequester metals and other pollutants from aqueous solutions in a metabolically-free manner [17]. In this way, biosorption is regarded as a passive process based on the affinity between the sorbate and the biomass, as opposed to bioaccumulation, which involves an active metabolic process [18]. The main advantages and disadvantages of biosorption are illustrated in Fig. 1 [8,19].

A wide variety of biological materials have been explored for heavy metal removal. Such biosorbents include low-cost, available and renewable materials, like: macroalgae, agricultural residues, industrial waste, animal materials, raw plants, sludge etc. [9,19–22]. Among the agricultural and forestry originating sorbents, *Phytolacca americana* biomass [23], olive tree pruning [24], Marula seed husk [16], cedar leaf [25], maize stover [26], peanut shells [27], cork waste [28] have been used in recent years for treating lead-containing wastewaters. Rapeseed is a member of the family *Brassicaceae* and has become a major crop harvested mainly for its animal feed and oil production potential. The major producers are European Union (20 Mt/yr), Canada (15 Mt/yr) and China (12 Mt/yr) [29]. In Romania, the total production of rapeseed has increased threefold between 2007 and 2014 [30]. To obtain one tone of biodiesel, 3.3 tons of rapeseed are needed, whereas approximately 2.1 tons is rapeseed meal [31]. Such high quantity of by-products and wastes needs to be handled in an environmentally safe way. An interesting alternative is its utilization as a low-cost biosorbent of pollutants from aqueous solutions [22,32–36]. Rapeseed is rich in specific macromolecules such as fatty acids and proteins [34], but also has lignin, cellulose and hemicellulose as major constituents. Such components offer a large variety and abundance of functional groups that can act as active sites on the surface of the biomaterial.

Over the years, biosorption experiments were carried out intensively in batch mode of operation [25–28,37]. Several papers reported lead biosorption by agricultural or vegetable biomass in dynamic conditions [24,38,39]. The use of a column in continuous operation is more practical at industrial scale, because of its simplicity and lower costs, while it can be more easily scaled-up from laboratory to the pilot and industrial scale [40].

The main objective of this study is to evaluate the potential of rapeseed biomass to remove lead ions from synthetic aqueous solution both in batch as well as continuous systems. The surface of the sorbent was studied by infrared (IR) spectroscopy and high resolution microscopy. The influence of initial concentration and contact time, related isotherm and kinetic models, and thermodynamic parameters were investigated in batch mode for a better understanding of the biosorption process. Column studies were done at different initial metal concentrations and several models were applied to analyse the breakthrough curves. In addition, the applicability of the biosorbent to remove Pb(II) ions from more complex matrices in a fixed bed column was verified by using a real industrial wastewater. To our best knowledge, this type of experiments used to test the biosorption affinity of rapeseed biomass have not been reported so far.

2. Materials and methods

2.1. Biosorbent preparation and characterization

Rapeseed (RS) originating from agricultural units around Iasi (Romania) was used in the present investigation. The biological material was prepared according to [36]. In short, the rapeseed was washed several times with Grade I water (Adrona Crystal E), dried at 40 °C for 24 h and crushed to obtain particle sizes between 0.1 and 0.2 mm.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Platinum ATR ALPHA Bruker, Germany) was used to determine the major functional groups on the surface of sorbent. Spectra before and after biosorption were recorded with a resolution of 2 cm^{-1} in the range 400–4000 cm^{-1}, with 128 acquisition scans.

The surface morphological features of loaded and unloaded rapeseed biomass were analysed using Scanning Electron

BIOSORPTION

Advantages

- Low metal concentrations (<100 mg/L)
- High efficiency
- Potential metal recovery
- Low cost
- Easy operation
- Reduced quantity of chemicals
- Reduced sludge handling

Disadvantages

- Few studies at pilot and industrial scale
- The possibility of increasing costs (wastes become commodities)
- Process mechanism of high complexity
- Disposal of biosorbent at the end of life

Fig. 1. Advantages and disadvantages of biosorption.