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Enhanced selective metal adsorption on optimised agroforestry waste mixtures

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HIGHLIGHTS

- Agroforestry wastes present good sorption capacities for a mixture of several metals.
- A mixture of biosorbents increases the total removal of metals.
- Optimisation of the biosorbent mixture proportions maximises metal removal.
- Recovery of metals can be achieved by treatment with weak acids.

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ABSTRACT

The aim of this work is to ascertain the potentials of different agroforestry wastes to be used as biosorbents in the removal of a mixture of heavy metals. Fern (FE), rice husk (RI) and oak leaves (OA) presented the best removal percentages for Cu(II) and Ni(II), Mn(II) and Zn(II) and Cr(VI), respectively. The performance of a mixture of these three biosorbents was evaluated, and an improvement of 10% in the overall removal was obtained (19.25 mg/g). The optimum mixture proportions were determined using simplex-centroid mixture design method (FE:OA:RI = 50:13.7:36.3). The adsorption kinetics and isotherms of the optimised mixture were fit by the pseudo-first order kinetic model and Langmuir isotherm. The adsorption mechanism was studied, and the effects of the carboxylic, hydroxyl and phenolic groups on metal–biomass binding were demonstrated. Finally, the recoveries of the metals using biomass were investigated, and cationic metal recoveries of 100% were achieved when acidic solutions were used.

1. Introduction

The processes of a wide variety of industries such as tanneries, plating, textile, mining, cosmetics, pharmaceutical and paper use many metals ions, including Cr(VI), Cr(III), Mn, Cu, Zn and Ni (Gupta et al., 2009). Once used, the compounds containing these metals can generate a wide range of wastewaters containing different pollutants. The amount of metal present in the wastewater is related to the operations developed in the industry. The removal of metals in effluent is required to attain the safe permissible metal limits and avoid the toxic and poisonous effects of these metals in the environment. For example, Cr(VI) has been recognised as a carcinogenic and mutagenic agent (Brauer and Wetterhahn, 1991), and the presence of Cr(III) at concentrations exceeding 5.0 mg/L may be toxic for aquatic life (Pérez Marín et al., 2009).

A wide range of physical–chemical, biological and oxidative technologies have been proposed to treat wastewaters containing metals (Nguyen et al., 2013). Among the different treatments available, adsorption is one of the most attractive technologies because of its versatility, simple design, ease of operation and high efficiency for pollutant removal (Rosales et al., 2012). However, the main drawback of adsorption is the high cost of efficient adsorbent materials. Activated carbon is the most widely studied adsorbent and has been widely applied in industry, providing high removal rates; however, its cost is a drawback in its general use (Crini, 2006). Thus, alternative low cost and biodegradable adsorbents are required. A suitable low-cost adsorbent requires a porous structure, mechanical and chemical stability and affinity for the target pollutants (Cobas et al., 2014). Recent approaches suggest

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Nomenclature

CA	cane pruning wine grapes
OA	oak leaves
RI	rice husk
GR	grapefruit peelings
FE	fern
ME	mixture fern, oak leaves and rice husk
OAM	optimised biosorbent mixture
q_{max}	model maximum achievable uptake by a system (mg/g)
b_L	langmuir model affinity between the sorbate and sorbent (L/mg)
R^2	linear correlation coefficient
K_F	Freundlich model binding capacity (mg/g)/(mg/L)$^{1/n}$
n_F	Freundlich model affinity between the sorbent and sorbate
K_{RP}	Redlich–Peterson model isotherm constant (L/g)
a_{RP}	Redlich–Peterson model constant $(\mathrm{L/mg})^{\beta_{RP}}$
β_{RP}	Redlich–Peterson model exponent
K_S	Sips model isotherm constant (L/g)
a_s	Sips model constant (L/mg)
β_S	Sips model exponent
k_1	Pseudo-first order rate constant (1/min)
k_2	Pseudo-second rate constant (g/(mg min))
C_e	concentration of metal solution at adsorption equilibrium (mg/L)
C_i	initial metal concentration of metal solution (mg/L)
q_e	equilibrium adsorption capacity of biosorbent (mg/g)
q_t	amount of metal adsorbed per unit of biosorbent at time t (mg/g)
t	contact time (min)
R	universal gas constant (J/(mol kg)
T	temperature (°C)
k_{id}	intra-particle diffusion rate constant (mg/(g h$^{0.5}$))

the utilisation of non-conventional adsorbents; natural clays (Iglesias et al., 2013; Padilla-Ortega et al., 2013), various industrial and agricultural materials such as hazelnut straws, peanut shell, banana peel, orange peel, walnut shell, rice husk and sawdust (Nguyen et al., 2013; Alothman et al., 2013; Ma et al., 2014; Park et al., 2008; Krishnani et al., 2008; Abdolali et al., 2014a) and forestry materials such as fern or oak leaves (Prasad and Freitas, 2000; Barriada et al., 2009) have been tested. These agroforestry materials have been mainly applied to the removal of a single or a couple of metals, while little attention has been paid to the simultaneous adsorption of multiple metals (Krishnani et al., 2008; Abdolali et al., 2014b; Hossain et al., 2014a).

The goal of this study is to ascertain the abilities of different agroforestry wastes as alternative low-cost biosorbents for the removal of wastewater streams containing different metals. First, the adsorption potentials of the agroforestry wastes were investigated. Then, the performance of the combination of the biosorbents were evaluated, and the composition of the mixed biosorbents was optimised using response surface methodology. Isotherms and kinetic data were also obtained. Finally, the adsorption mechanism was studied, and biosorbent recovery was evaluated.

2. Experimental

2.1. Reagents

A stock solution containing Cr, Cu, Mn, Ni and Zn was obtained by dissolving the metal salts in water. $ZnCl_2$, $CuCl_2{\cdot}2H_2O$, $MnCl_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ were purchased from Merck, and potassium dichromate ($K_2Cr_2O_7$) was obtained from Sigma–Aldrich. All the used chemicals were reagent grade.

2.2. Agroforestry wastes

The materials used in the study were agriculture and forestry wastes. Cane pruning wine grapes (CA), fern (FE), eucalyptus bark (EU), oak leaves (OA), grapefruit (GR) and rice husk (RI) were provided by local suppliers. The wastes were washed three times with distilled water, dried in an oven at 60 °C for 24 h and then grounded to pass through a 1-mm sieve before use.

2.3. Metal adsorption by biosorbents

Adsorption studies were performed individually for each biosorbent in Erlenmeyer flasks (250 mL) containing 1 g of biosorbent with a working volume of 150 mL. The experiments were carried out at 25 °C and 150 rpm for 4 h. A synthetic wastewater was prepared containing a mixture of the different metals. The initial concentration of each metal in this synthetic wastewater was 50 mg/L, resulting in a total metal content of 250 mg/L.

The metal adsorption assays using a mixture of untreated biosorbents were performed under the same conditions with a final mass of 1 g. Kinetic and isotherm studies were carried out under the same conditions as previously described. For the isotherms assays, the concentration of each metal in the synthetic wastewater ranged from 6–400 mg/L.

2.4. Adsorption process mechanism

The adsorption mechanism was evaluated by modifying the surfaces of the biosorbents using different selected chemical agents. Chemical modification methods could activate/deactivate the available binding sites on the biomass surface (Abdolali et al., 2014a). To evaluate the adsorption mechanism, the chemical blocking of functional groups was applied. The esterification of carboxylic acids with methanol-HCl (HM-ME) and the methylation of hydroxyl and phenolic groups with formaldehyde (FO-ME) were carried out. The carboxylic acids present in the biosorbents were esterified by alcohols in the presence of a suitable acidic catalyst (HCl) according to Gardea-Torresdey (1990). The modification of the biosorbents with formaldehyde was performed according to Deshkar et al. (1990).

2.5. Recovery of the metals

After adsorption, the biosorbent was recovered by filtration and dried in a stove at 60 °C for 24 h. The biosorbent loaded with metals was then treated with an eluent (water, HCl 0.1 N and HNO_3 0.1 N). Desorption tests were performed using 1 g of the used biosorbent in 150 mL of the eluent. After 120 min at 150 rpm, the samples were filtered, and the pH and metal concentrations in the liquid were determined.