Bioresource Technology 128 (2013) 36–43

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Uptake of gold (III) from waste gold solution onto biomass-based adsorbents organophosphonic acid functionalized spent buckwheat hulls

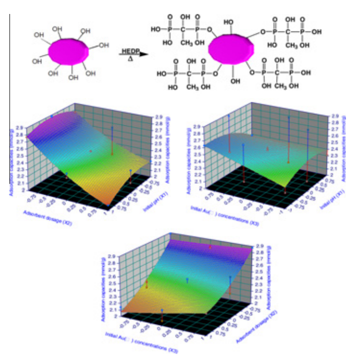
Ping Yin *, Mingyu Xu, Rongjun Qu *, Hou Chen, Xiguang Liu, Jiang Zhang, Qiang Xu

School of Chemistry and Materials Science, Ludong University, Yantai 264025, PR China

HIGHLIGHTS

- ▶ Feasibility of novel functionalized buckwheat hulls OPA-BH for gold uptake was confirmed.
- ▶ The low-cost biosorbent had very high adsorption capacity for Au(III).
- ▶ The biosorption process optimization was performed using response surface methodology.
- ▶ Desorption and regeneration studies were conducted to evaluate this adsorbent efficiency.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 July 2012
Received in revised form 9 October 2012
Accepted 11 October 2012
Available online 23 October 2012

Keywords:
Biomass-based adsorbent
Buckwheat hulls
Organophosphonic acid
Functionalization
Au(III) uptake

ABSTRACT

Novel biomass-based adsorbents organophosphonic acid functionalized spent buckwheat hulls (OPA-BH) with 60 mesh were successfully employed to adsorb Au(III) ions from simulated wastewater. The adsorption kinetics and isotherms both in unary ion system and in ternary ions system were investigated, and the applicability of the Langmuir, Freundlich and extended Langmuir isotherm models has been tested for the equilibrium. The process optimization was also conducted by using response surface methodology (RSM), and the maximum adsorption capacities reached 2.84 ± 0.01 mmol/g under the optimum process conditions. Furthermore, the regeneration capacities of OPA-BH were investigated by using the eluent solutions of 0.0–5.0% thiourea in 0.1 mmol/L HCl, and the results showed that the adsorption capabilities for OPA-BH were ranged between 0.77 mmol/g and 0.85 mmol/g after three cycles of adsorption–desorption processes. The research results showed that OPA-BH was favorable and useful for gold adsorption, and the high adsorption capacity and good reproducibility make it a good promising material for the precious metal uptake.

1. Introduction

The demand for gold, one of the precious metals used as a global currency, has shown an increasing trend because of its increasing uses in industry. The unique chemical and physical properties offered by gold are increasingly being sought for use in a growing number of industrial and medical applications. Therefore, it is very necessary to recover gold from industrial scraps and wastewater (for example, the scraps from electronic devices containing gold, such as cellular phones and personal computers). Then, the effluents from these scrap industry containing precious metal gold have attracted considerable attention not only because it is a precious metal and a conducting material but also because of its use in various chemical and electrochemical applications (Fujiwara et al., 2007; Nguyen et al., 2010).

More attentions have been focused on the methods for recovery and reuse of metal ions. Adsorption is highly effective, economical and a widely used method for metals ions uptake from different aqueous solutions (Stafiej and Pyrzynska, 2007; Feng and Aldrich, 2004). Recently, the search for low-cost biomass-based adsorbents that have metal-binding capacities has been intensified. Agricultural

* Corresponding authors. Tel.: +86 535 6696162; fax: +86 535 6697667.
E-mail addresses: yinping426@163.com (P. Yin), rongjunqu@sohu.com (R. Qu).

0960-8524/$ - see front matter
http://dx.doi.org/10.1016/j.biortech.2012.10.048

residuals such as spent-grain rice, barley husk, and rice husk etc. are one kind of the rich sources for low-cost adsorbents (Lu and Gibb, 2008; His et al., 2011). Buckwheat has become popular as a kind of healthy food, since it was reported that its seeds contain many biologically active compounds. As one kind of agricultural residuals, buckwheat hulls are rich in cellulose, and offer many functional groups such as hydroxyl, carboxyl and amino groups, which can bind metal ions. Therefore, these biopolymers are being considered ideal bioadsorbents for heavy metals removal from wastewater (Li et al., 2012). Spent buckwheat hulls are disposed as waste during buckwheat production, they have not any commercial value and will exert environmental burden as a result of decay. Then, they are eco-friendly and low-cost source of readily available adsorbent, and they have been investigated and proved effective (Wu et al., 2012). However, many of the naturally available adsorbents have low metal removal and slow process kinetics. Thus, it is necessary to develop innovative inexpensive adsorbents with good affinity towards metal ions. Surface functionalization technology has been proven to be effective (Wu et al., 2012). According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for coordinating with ligands that have more or less electronegative donor atoms. The bonding between soft acids and bases seems to be primarily covalent in nature, thus a strong interaction occurs between large metal ions with high electronegativity (for example, Pt, Au and Pb) and the most polarizable bases. In general, functional groups containing S and N donor atom interact strongly with soft acids like precious metals (Fujiwara et al., 2007; Kim and Tudino, 2010). Phosphonic acid groups can provide several oxygen atoms to coordinate metal ions, which can be utilized to remove heavy metals from bleaching solution in the paper, pulp and textile industry (Latham et al., 2009). Oxygen is a hard base while gold is a soft acid according to HSAB, therefore only a few researches on the interaction between these two elements were reported (Gardea-Torresdey et al., 2002; Yin et al., 2011), they found that the carboxyl group/phosphonic acid group play some role in the binding of Au(III), and higher gold (III) binding at low pHs. If phosphonic acid group is grafted on the solid matrix, this kind of chemical modification can overcome the problems of its being soluble in water and being difficult to recover, and can enhance adsorption kinetics properties, then it can be used in adsorption of metal ions from aqueous solutions. Moreover, the toxicity of phosphonates to aquatic organisms is low, and human toxicity is also low which can be seen in the fact that phosphates are used to treat various diseases (Nowack, 2003). Buckwheat hulls is a kind of agriculture residues, it is non-toxic and biodegradable biomass. Therefore, organophosphonic acid-functionalized spent buckwheat hulls can be used as low-cost bioadsorbent with high efficiency for water purification and help industries reduce the cost of waste disposal.

So far, to our knowledge, the adsorption investigation of organophosphonic acid-functionalized spent buckwheat hulls has seldom reported. The objective of the present work was to explore low-cost agricultural residues organophosphonic acid-functionalized buckwheat hulls with high adsorption capacity and reproducibility for Au(III) ions from waste gold solution. The relevant adsorption kinetics and isotherms have been investigated, and response surface methodology (RSM) has also been employed to optimize the adsorption process parameters. RSM allows users to gather large amounts of information from a small number of experiments, and it is also possible to observe the effects of individual variables and their combinations of interactions on the response by using RSM (Ghorbani et al., 2008). For better understanding of different stages of biosorption at different metal concentration, pH and sorbent dosage, RSM was used to optimize gold uptake. Moreover, the recycling of OPA-BH for Au(III) ions uptake was investigated.

2. Methods

2.1. Materials and methods

The spent buckwheat hulls were collected from a buckwheat production site in the suburbs of Yantai, Shandong Province, and they were washed with generous amounts of deionized water, dried at 50 °C, and then ground in a mill to pass through a 60 mesh sieve to obtain a uniform particle size for further processing. For surface functionalization, 10.0 g of powdered biomass was agitated at 60 °C for 24 h in 50 mL of 20.0% HEDP (1-hydroxyethylidenediphosphonic acid) solution. HEDP is one of the most important phosphonic acid, which contains two C–PO(OH)$_2$ groups (please see Supplementary Fig. S1, available online in the supplemental materials), thus the esterification reaction could be carried out and the remaining phosphonic acid group could chelate with metal ions. The resulting biomasses were filtered and dried, then, the treated sample was thermochemically reacted for 4 h by elevating oven temperature at 120 °C. The products obtained were mixed in deionized water for 30 min, filtered and washed with deionized water.

Organophosphonic acid functionalized buckwheat hulls (OPA-BH) were dried in the oven. Finally, the functionalized hulls were vacuum oven dried at 45 °C for 48 h. The thermally treated sample was cooled to the room temperature and then stored for the following adsorption experiments. Esterification reaction efficiency is the percent amount of organophosphonic acid that is attached on the structure of BH, and the relative measure process that reported by Altun and Pehlivan (2012). OPA-BH products were soaked into pure water for 30 min and the pH of the system was adjusted, the treated samples were filtered and washed with pure water. Then (OPA-BH) filtrated and 0.1 M NaOH solution was added. Remaining NaOH in the solution phase was titrated with 0.1 M HCl. All other reagents utilized in the experiments were analytical grade and used without any further purification, and all solutions were prepared with deionized water. Mimicked waste gold solution (1 g/100 mL) was prepared by dissolving chloroauric acid ($HAuCl_4$) in distilled water. The aqueous solution was diluted with distilled water to obtain the working solutions of desired concentration. The pH of solution of Au(III) was adjusted with hydrochloric acid aqueous solution (1 mol/L) and sodium hydroxide aqueous (1 mol/L). However, those pH values of solution of the other metal ions were adjusted with ammonium acetate/nitric acid solutions. Infrared spectra (FT-IR) of samples were reported in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}, by accumulating 32 scans using a Nicolet MAGNA-IR 550 (series II) spectrophotometer. KBr pellets were used for solid samples. The inductively coupled plasma (ICP) analysis was carried out on a Shimadzu ICPE-9000 spectrometer. The concentration of Au(III) ions were determined using a 932-model atomic absorption spectrometer (GBC-932A, made in Australia), equipped with air–acetylene flame.

2.2. Adsorption experiments for transition metal ions

Saturation adsorption experiment was employed to determine the adsorption amounts of OPA-BH for different kinds of metal ions, and they were carried out with shaking 30.0 mg of the adsorbent with 20.0 mL of metal ion solution (2.0 mmol/L). The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 25 °C.

The adsorption amount was calculated according to the Eq. (1)

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$