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Recovery of Au(III) from an aqueous solution by aminopropyltriethoxysilane-functionalized lignocellulosic based adsorbents

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ABSTRACT

Lignocellulosic coconut pith (LCP) was functionalized with 3-aminopropyltriethoxysilane (APS) towards preparing aminopropyltriethoxysilane-functionalized lignocellulosic coconut pith (APS-LCP) adsorbents for high adsorption affinity towards Au(III) ions. The functionalization was confirmed by morphological, functional groups and thermal analyses. The Au(III) adsorption results show that the APS-LCP possessed much better Au(III) adsorption than LCP and both exhibited endothermic process. The Au(III) adsorption isotherm data fitted well to the Langmuir isotherm having the maximum adsorption capacity of 215.68 mg g^{-1} and 261.36 mg g^{-1}, respectively, for the LCP and APS-LCP at 30 °C. The kinetic model analysis showed that the overall adsorption process was controlled by film diffusion, while the active site chemical interactions (e.g. ion exchange, chelation and reduction) were best described by the pseudo-second order kinetic model. Adsorption-desorption experiment revealed that the APS-LCP could be regenerated with minimum loss of the adsorption capacity. These results demonstrate the potential application of lignocellulosic materials as adsorbents through an appropriate modification for adsorptive recovery of Au(III) ions from an aqueous solution.

1. Introduction

Aurum (Au) or gold is a noble metal which has been used in many fields such as jewelry, biomedicine, aerospace construction, electric and electronic devices, medical instruments, and catalysts in various chemical processes [1,2]. Due to its vast applications, high demand and limited resources, its recovery from various wastes has gained considerable attention. Several processes have been developed for Au recovery including chemical precipitation, membrane filtration, electrolysis, ion-exchange, extraction and adsorption [3]. However, some of these processes may require or release toxic chemicals, incomplete removal and high capital cost [4]. Therefore, due to safety issues and ineffectiveness, more cost-effective and environmentally benign technologies for Au selective recovery have been developed [1]. Adsorption is known as the most promising technology for Au recovery because it is low-cost, simple operation, no or little organic solvents and high efficiency [2]. In addition, the adsorbent used can be made a specialty towards certain pollutant and even now, researches of alternative adsorbents still remain a priority in the field of adsorption.

In solution, Au presence as anionic chloro-aurate complexes, therefore, cationic ionized functional groups of adsorbent is preferred for the effective adsorption. Ion-exchange resins and polymeric materials containing selective functional groups are widely applied and are excellent for recovering precious metals (Table 1).

Adsorption using solid resins/polymers however is not very economical due to the usage of high cost commercial resins and leakage of extractant from the resins during the usage [13]. More importantly, processing and producing the resins provide an easy route for toxic compounds to enter the environment. Due to environmental and economic issues, these petroleum-based resins should be replaced by alternative renewable biomaterials such as cellulose, chitosan, tannin, agro/industrial residues, and living biomass [13,15]. Agricultural lignocellulosic biomasses are very interesting materials and have been widely studied as alternative low-cost adsorbents due to voluminous availability and ease of chemical modifications. The presence of oxygenated functional groups from lignin, hemicellulose and cellulose structures is reported in many literatures that promote chemical interactions with various metal ions during the adsorption process [29,30]. Modifications through crosslinking and functionalization of the raw materials are commonly applied to improve the adsorption

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Table 1
Au(III) adsorption capacity of various adsorbents reported in the literatures.

Adsorbent matrices	Functionalized substances	Q_{max} (mg g^{-1})	References
i) Resins/Polymers			
Acrylic	Dimethylaminobenzaldehyde	97.75	[5]
Triazine polyamine polymers	–		[6]
a) Triazine-ethylenediamine		a) 548	
b) Triazine-triehtylenetetra-mine		b) 1003	
c) Triazine-pentaethylene hexamine		c) 1086	
N-2-(2-pyridyl) ethylchitosan (PEC)	–	965.1	[7]
1-methylimidazole (gel)	–	11.25	[8]
2-mercapto-1-methylimidazole (gel)	–	4.67	
Polystyrene	3-amino-1,2,-propanediol	–	[9]
Amberjet™ 4400	–	427.8	[10]
Amberlite XAD-7HP	–	60	[11]
Bonlite BA304	–	110	
Purolite A-500	–	147	
ii) Biomaterials			
Humic acid	–	90.9	[12]
Alginate	Aliquat-336	176.1	[13]
Cellulose	Aminomethyl pyridine	537.5	[14]
Cellulose acetate fiber	Acetate	110	[15]
Cellulose	Taurine	34.5	[16]
Persimmom tannin	N-aminoguanidine	1753	[17]
Persimmom tannin	Tetraethylene pentamine	1168	[18]
Kraft mill lignin	–	1181.8	[19]
Chitosan	Glutaraldehyde	990.1	[2]
Chitosan	Graphene oxide (GO)	1076.6	[2]
Crosslinked-cellulose	–	1491	[20]
Rambutan peel	Polyphenol	2530	[21]
Persimmon tannin (crude)	–	1142.4	[22]
Crosslinked-persimmon tannin	–	1516.6	[22]
Corynebacterium glutamicum	Polyethylenimine	361.8	[10]
Chitosan	Glycine	169.9	[23]
Grape waste	–	1962	[1]
Alfafa biomass (*Medicago sativa*)	–	–	
iii) Others			
Magnetic nanoparticles (MNP-G3)	Ethylenediaminetetraacetic acid	3.6	[24]
Silica gel	Diethylenetriamine (DETA)	417.6	[25]
Fine-tuning conjugate adsorbent	6-((2-(2-hydroxyl-1-naphthoyl)hydrazono)methyl) benzoic acid	203.42	[26]
Graphene oxide (GO)	–	146.2	[2]
Mesoporous silica	Tannin	642	[27]
Activated carbon	–	170.6	[20]
MCM-41	APTES[a]	275	[28]
	MPTES[b]	195	

[a] 3-aminopropyl-trimethoxysilane.
[b] 3-mercaptopropyl triethoxysilane.

capacity and selectivity towards targeting metal ions. Ligands containing nitrogen, sulfur and oxygen donor atoms are preferred in the adsorption of precious metals because of hard and soft acids and bases (HSAB) principle [31]. Among of that, ligands with nitrogen functional group such as aminomethyl pyridine [14], polyethylenimine [10], and tetraethylene pentamine [17] show very promising adsorption towards Au(III) ions. This is because the nitrogen atom can be easily protonated in acidic condition and forms a stable binding with chloro-Au complexes [17,32,33].

By taking all the considerations, this study was proposed to demonstrate a green adsorption pathway for Au recovery. Lignocellulosic coconut pith (LCP) was used as a raw material in which it was functionalized with 3-aminopropyltriethoxysilane (APS) to enhance Au(III) adsorption performance. The APS was chosen as a functionalization agent due to the presence of a terminal nitrogen group in its molecular structure which is expected to have high binding affinity towards Au (III). To our knowledge, investigations on organosilane-functionalized lignocellulosic materials specifically for Au(III) recovery have not been reported. The organosilane-functionalization adsorbents were mostly conducted onto silica materials. Our previous work on organosilane-functionalized lignocellulosic materials was focused on the mercury ion adsorption [34–37]. In this work, the APS-functionalized lignocellulosic coconut pith (APS-LCP) adsorbents were prepared and characterized. The Au(III) adsorption characteristics namely adsorption isotherm and kinetics, adsorbent regenerability and adsorbent selectivity were investigated and presented in detail.

2. Materials and methods

2.1. Materials

The lignocellulosic of coconut pith (LCP) was supplied by a local company (T&H Coconut Fiber Sdn. Bhd.). Sodium hydroxide (NaOH, 99%), nitric acid (HNO_3, 65%), hydrochloric acid (HCl, 37%), toluene (99.99%) and ethanol (absolute, 99.99%) were purchased from Merck (Germany). 3-aminopropyltriethoxysilane (APS, 99%) was purchased from Power Chemical Corporation (China). Aurum (III) chloride salt (99%) was purchased from sigma-Aldrich. All chemicals were of analytical grade except APS which was of industrial grade. The chemical was used directly without any purification.

2.2. Adsorbent preparation and functionalization procedures

The LCP was washed, dried, ground and sieved for particle size range between 75 μm to 150 μm. The LCP sample was then dewaxed by the Soxhlet-extraction method using a toluene-ethanol solvent mixture (2:1, v/v) for 48 h. Thereafter, the material was separated and dried in an oven at 50 °C overnight.

The functionalization of LCP with APS was carried according to the previous studies [34,35]. Firstly, 0.1 M of APS was pre-hydrolyzed in an ethanol/water mixture. Then, 0.5 g of LCP was added into the mixture and stirred at room temperature (30 °C) at 200 rpm. After 2 h of stirring, the mixture was then placed in an oven at 60 °C and left overnight. The APS-LCP was then washed with an ethanol/water mixture, dried in an oven at 60 °C and further dried in a vacuum oven at 30 °C for 5 h.

2.3. Characterization procedures

The scanning electron microscope, SEM (JEOL model JSM-6390LV, Japan) was used to examine the morphology of the adsorbents. The adsorbent was mounted on a stainless steel stab and coated with gold to improve conductivity for a better quality of SEM images. The presence of functional groups on the adsorbent surface was analyzed using a Fourier transform infrared (FTIR) spectrometer (Perkin Elmer model 2000, USA) by the KBr disk method. The test for thermal stability and degradation characteristics of materials before and after functionalization were carried out using a thermogravimetric analyzer, TGA (Perkin-Elmer model Pyris TGA7, USA). The experiment was conducted under nitrogen atmosphere with a flow rate of 40 mL min^{-1}. The degradation characteristic was monitored from temperatures of (30 to 900) °C with a heating rate of 20 °C min^{-1}. The X-ray diffraction (XRD) spectrum of the adsorbent surface was recorded by using an X-ray diffractometer (Rigaku model SmartLab, Japan) equipped with CuKα radiation source.