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Selective adsorption of metallic complex using polyaniline or polypyrrole

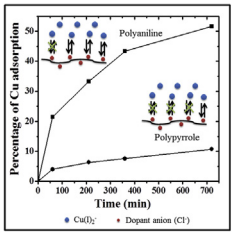
Irela Santos Sauceda [a], María Mónica Castillo Ortega [a, *], Guillermo Tiburcio Munive [b], Jesús Manuel Quiroz Castillo [c], Teresa del Castillo Castro [a], Martín Antonio Encinas Romero [b], Manuel Aguilar Vega [d], José Zeferino Ramírez [a], Luis Sergio Quiroz Castillo [e]

[a] Departamento de Investigación en Polímeros y Materiales, Universidad de Sonora, Rosales y Blvrd. Luis Encinas, C.P. 83000, Hermosillo, Sonora, Mexico
[b] Departamento de Ingeniería Química y Metalurgia, Universidad de Sonora, Rosales y Blvrd. Luis Encinas, C.P. 83000, Hermosillo, Sonora, Mexico
[c] Universidad Estatal de Sonora, Ley Federal del Trabajo S/N, C.P. 83100, Hermosillo, Sonora, Mexico
[d] Unidad de Materiales, Centro de Investigación Científica de Yucatán, Calle 43 No. 130 Col. Chuburná de Hidalgo, C.P. 97200, Mérida, Yucatán, Mexico
[e] Department of Materials Engineering, University of British Columbia, 309-6350 Stores Road, Vancouver, B.C., V6T 1Z4, Canada

HIGHLIGHTS

- The preparation of (M) composites, coated with PAni or PPy was performed.
- The composites present good environmental stability.
- M-PAni is an effective adsorbent for the recovery of a metallic complex of copper.
- M-PPy is a selective material recommended for the recovery of gold, not for copper.
- Both composites obey the Langmuir isotherm model, a monolayer adsorption process.

GRAPHICAL ABSTRACT



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ABSTRACT

The preparation of composites of cellulose acetate, triphenyl phosphate and poly (acrylic acid) (M), coated with polyaniline (M-PAni) or polypyrrole (M-PPy), including tests of the adsorptivity of complexes of copper-iodide, are presented in this work. Characterization of M-PAni and M-PPy by FT-IR and TGA before and after being exposed to natural weathering conditions are done to study the effects that environmental conditions have on them. In solutions with Cu only, the M-PAni presented 51.6% Cu adsorption and M-PPy presented 10.7%. SEM analysis, EDS, XPS and ATR-FTIR of M-PAni and M-PPy before and after of Cu adsorption are included. In the presence of gold-iodide complex, M-PAni shows 47.4% Cu adsorption, six times higher than the M-PPy, 7.2%; this result is attributed to better interaction between the PAni and the copper-iodide complex than PPy and the copper-iodide. The adsorption equilibrium data of copper-iodide complex fits the Langmuir isotherm model for both M-PAni and M-PPy, suggesting the formation of an adsorbed monolayer. Desorption process for Au is more effective in the two materials, 34.1% with M-PAni and 86.6% with M-PPy, than for Cu with 1.0% and 2.6% respectively.

* Corresponding author.
E-mail address: monicac@guaymas.uson.mx (M.M. Castillo Ortega).

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The present method, which uses iodide as a single leaching agent for Au and Cu and M-PAni and M-PPy as adsorbents is recommended. These composites are suitable selective materials.

1. Introduction

Currently, the recovery and extraction of Cu from ore involves different methods such as leaching by sulfuric acid, flotation, solvent extraction, deposition and electrolysis; as well as different materials have been proposed. For example, the adsorption process using activated carbon [1], rubber (*Hevea brasiliensis*) leaf powder [2], macroporous chitosan membrane [3] and garden grass [4] have been studied for the removal of copper cyanide species and Cu (II) ions from aqueous solutions. On the other hand, Au ores which were subject to iodide/iodine leaching and the recovery of Au from iodine–iodide solutions using strong base anion exchange resins have been investigated [5,6].

Interesting materials for application in this field are the electroconductive polymers, such as polyaniline (PAni) and polypyrrole (PPy), which have ion exchange properties [7–9]; therefore, are excellent candidates for potential application in the removal of metals from aqueous solutions. However, because of poor mechanical properties and processing difficulties, as a result of the high conjugation, strong electrostatic interactions between chains, and in some cases, the aromatic nature of the polymers, their use in commercial applications has been limited. A possible solution to the above is the development of composite materials, where a layer of a conductive polymer acts as an active component and the matrix provides the desirable mechanical properties.

The use of composite materials of electroconductive polymers for the removal of metals has been reported. For example, polyaniline modified graphene oxide (PANI/GO) composites for the selective adsorption of uranium(VI) or Cr(VI) [10,11], polyacrylonitrile/PPy core–shell structure nanofibers for the removal of Cr(VI) from aqueous solution [12]. The adsorption of chromium compounds from solutions by a composite of PAni/polyethylene glycol [13]; PPy/sawdust and PAni/sawdust were used as effective adsorbents for the removal of heavy metals, anions, color and COD (chemical oxygen demand) from mill paper wastewater [14]; batch sorption system using eco-friendly conducting polymer/biopolymer composites viz. PAni/chitosan and PPy/chitosan as adsorbents were investigated to ensnare F^- ions from aqueous solutions [15]; PPy coated on the sawdust for the removal of Zn (II) ions from aqueous solutions [16]; Hg(II) ions and Cr(VI) anions were selected to evaluate the adsorption properties of PAni/humic acid [17]; kapok fiber-oriented PAN nanofibers were developed and used as the adsorbent to remove Cr(VI) [18]; glycine doped PPy was used for the removal of Cr(VI) [19]; the composite of PAni and reduced graphene oxide for the adsorption of Hg (II) in aqueous solutions [20]; PAni/alumina and PPy/alumina composites for the removal of F^- ions from aqueous solution by the batch sorption method [21], and PAni nanofibers assembled on alginate microsphere for Cu^{2+} and Pb^{2+} uptake [22]. Broadly, different composites containing electroconductive polymers, used for water purification, have been reported [23]. In a previous work, we reported a comparative study of cellulose acetate membranes coated with PAni or PPy for adsorption and subsequent desorption of a gold-iodide complex, as well as the preparation and characterization by SEM, XPS, and mechanical and electrical properties analyses [24].

This study is focused on test the cellulose acetate composites coated with PAni (M-PAni) or PPy (M-PPy) for the adsorption-desorption of Cu and Cu–Au mixtures, from aqueous iodine-iodide solutions. Also we evaluated the natural weathering of the M-PAni and M-PPy composites by FT-IR and TGA to propose the use of the composites in the mining sector, as a less polluting process than those currently used and with good selectivity for Cu–Au mixtures. The use of M-PAni and M-PPy is a good alternative because it involves a single leaching and avoids the use of cyanide and sulfuric acid, typical leaching agents with high toxicity for Au and Cu, respectively.

2. Materials and methods

2.1. Materials

The materials used in this study included cellulose acetate (CA) powder, 39.7 wt % acetyl content, average $M_n = 50{,}000$ (Aldrich); poly(acrylic acid, sodium salt) (PAA) 35 wt % solution in water, $M_w = 15{,}000$ (Aldrich); acetic acid, glacial ACS (Meyer); triphenyl phosphate, $\geq$ 99% (TPP) (Aldrich); ammonium persulfate (J.T.Baker); hydrochloric acid (Meyer); ferric chloride ACS (Fermont); aniline 99% (Aldrich), and pyrrole 98%, (Aldrich), were distilled under vacuum in nitrogen atmosphere before use. Potassium iodide ACS (Meyer); iodine ACS, $\geq$ 99.8% (Meyer); copper, powder, spheroidal, < 10 μm, 99% (Aldrich), gold powder 99.99% pure. All other reagents were used as received.

2.2. Preparation of CA composite coated with PAni or PPy

CA composites modified with PAA and plasticized with TPP (M) coated with polyaniline (M-PAni) or polypyrrole (M-PPy) were obtained using the procedure reported previously by us [24], with a modification in the polymerization time of the aniline and pyrrole, 5 min and 15 min in the oxidant solution, respectively.

The preparation of the membranes was using the phase inversion method. For its coating with PAni or PPy, solutions of the monomers and oxidant agent were used.

2.3. Natural weathering of the composites

The test site was located in the rural/urban semiarid atmosphere of Hermosillo city (29° 05′ N, 110° 57′ W; 282 m. a.s.l.), 100 km off the Gulf of California on the Pacific coast. The membranes, M-PAni and M-PPy, of 1 cm^2 were exposed on a stationary rack fixed to the laboratory roof at the site latitude angle (35°). Samples were taken and characterized at 30 days during the experimental period (May-June 2013). On-site temperature and humidity was recorded every hour by a data logger (HOBO® Onset Computer Corp.) placed on the rack close to the samples. Location irradiance data during the experimental period was obtained from the Solar Monitoring Station in the Agriculture Department (Universidad de Sonora). The UV irradiation (290–385 nm) was estimated using the equation proposed by Al-Aruri [25], which is an empirical relationship between global radiation and global ultraviolet solar radiation components. The conditions of exposure of the composites to humidity, UV radiation and temperature are given in Table 1.