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Biosorbents from *Mangifera indica* L. Peel for the Recovery of Gold from Electronic Waste

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ABSTRACT

Mango (*Mangifera indica* L.) peel, a food processing waste, is rich in polyphenols and polysaccharides, two substances that have previously been linked in the selective recovery of gold from metals solution. This study was carried out to develop biosorbents from green and ripe mango peel for the retrieval of gold from electronic waste (e-waste). Biosorbents were produced by cross-linking the components of mango peel through acid treatment. The gold from the mixture of metals leached from the e-waste was recovered using the cross-linked and untreated mango peel. Fourier transform infrared (FTIR) spectroscopy was employed to confirm cross-linking and to monitor the adsorption of gold. Scanning electron microscopy (SEM) was performed to characterize the surface of the biosorbents. Incineration was conducted to separate gold from the biosorbent. The results of the FTIR analysis revealed an increase in the intensity of the peak for C=O and the appearance of the signal for C-O-C, suggesting cross-linking. The FTIR spectra of the untreated and cross-linked biosorbents also showed more intense peak for C=O, which may be due to the oxidation of OH groups as gold ions are reduced. The SEM revealed increase in the roughness of the surface of the biosorbents, presumably as the result of gold deposition. Although all biosorbents were able to capture gold from the leachate, the cross-linked green mango peel appeared to be the most effective.

Keywords: biosorbent, agricultural waste, electronic waste, mango peel.

INTRODUCTION

Electronic waste (e-waste) or waste electric and electronic equipment (WEEE) pose disposal challenge worldwide. The amount of e-waste will likely increase due to the progress in electronics and communication technology that encourages the development of new products and the discarding of old models or items that are out-of-order. It was reported that 41.8 million metric tons of e-waste was generated in 2014 worldwide, and it was projected to increase to 50 million metric tons by 2018 (Balde et al., 2015). These products contain various metals, including precious metals. Citing a report published in 2008, Akcil et al. (2015) reported in a review article that scrap printed circuit boards (PCBs) contain the following nonprecious metals (wt%): 12 Fe; 10 Cu; 7 Al; 1.2 Pb, and 0.85 Ni, as well as precious metals (ppm): 280 Ag and 110 Au. In 2015, the Philippines produced 243 kilotons of e-waste, which represented a 61.2% increase from 2010 (Honda et al., 2016). If disposed of improperly, the toxic heavy metals content of these e-waste may leach into the environment, leading to pollution. When disposed of in landfills, the precious and nonprecious metal resources will be unavailable for reuse. Thus, recovery of metals from this waste is the best option to avoid environmental pollution and to promote the sustainable use of nonrenewable mineral resources. The current approaches in the recovery of metals from e-waste, unfortunately, utilize harmful chemicals such as cyanides (Akcil et al., 2015). Therefore, the search for alternative and greener methods for the mining of metals from these wastes is highly warranted. Biosorption is an alternative strategy in the extraction of metals, including precious metals from a solution using materials derived from biomass such as seaweeds, fungi and bacteria, eggshell membrane, and chitosan (Won et al., 2014). Persimmon peel, persimmon tannins extract, and modified tannins (Fanet al., 2014; Inoue et al., 2015; Yi et al., 2016) and sugarcane bagasse (Rubcumintara, 2015) have been shown to be effective in the selective biosoprtion of gold. Cross-linked polysaccharide gels (Pangeni, Paudyal, Abe, et al., 2012a) and modified chitosan (Donia et al., 2007) have also been used. Over 90% recovery was reported in these studies.The mechanism for the biosorption of gold in solution and its subsequent reduction to metallic gold on different biosorbents has previously been described. Polyphenols, such as tannins, have hydroxyl groups that can reduce gold ion in solution to elemental gold (Kawakita et al., 2009). According to Inoue et al. (2015), the selective reduction of gold was due to the higher oxidation reduction potential of gold ions compared to other metals. Agricultural wastes, such as fruit and vegetable peels, contain substances like tannins and polysaccharides that may be developed into biosorbents for precious metals recovery. A study of the chemical constituents and antioxidant properties of several fruit peels revealed that the total polyphenols in mango peel is 11,233.70±450.75 mg gallic acid equivalent/100 g, while calamansi (*Citrofurtunella microcarpa*) and plantain banana (*Musa acuminata × balbisiana Colla* (ABB Group) cv. "Saba") have only about 2,500 and 700, respectively (Samonte & Trinidad, 2013). Results from our laboratory showed that among several fruit and vegetable residues, mango peel afforded distilled spirits extracts with the highest antioxidant activity (Ortinero et al., 2020). Thus, mango peel, one of the main agricultural wastes produced in the Philippines, is a potential selective biosorbent for gold. Here we report the development of biosorbents from mango peel and their subsequent use in the recovery of gold from e-waste.

EXPERIMENTAL METHODS

Materials

Analytical grade or of the highest purity available chemicals were used in the study. They were used as received without further purification. All glassware were acid-washed and rinsed with distilled water and were dried afterwards. A total of 507.53 g of pieces of e-waste from various devices, including computer parts (CPU, monitor and keyboards) radio and karaoke sets, cellphones, and memory and SIM cards were obtained from electronic repair shops in Nueva Ecija, Philippines. Ripe and green (unripe) mango peelings were collected from a fruit market in Nueva Ecija, Philippines.

Leaching of metals from waste printed circuit boards (PCBs)

Size reduction of the collected pieces of e-waste was done according to the method of (Sheng & Etsell, 2007). The method of (Fan et al., 2014) was then modified and applied. A 500 g sample of e-waste previously leached in the nitric acid solution was soaked in 1 L aqua regia until no visible change was taking place. The leachate containing gold and other metals was used for biosorption experiments.

Development of biosorbents from agricultural waste

Peelings of ripe and green (unripe) mangoes (carabao variety) were collected from a public market. Cross-linking of the components of the peelings was done according to the method of (Pangeni et al., 2012b). The raw mango peelings were ground and added with concentrated sulfuric acid. The mixture was stirred for 24 hours at 100 ^{o}C. The cross-linked products were recovered by filtration, neutralized with sodium bicarbonate, and washed with distilled water. After oven-drying for 24 hours, the products were pulverized.

Recovery of gold from aqua regia solution

Recovery of gold from aqua regia was performed using the method of (Yi et al., 2016) with some modifications. The biosorbent was added to the metals solution and the mixture was agitated for 14 hours at 30 ^{o}C. The biosorbent with gold was recovered through filtration and oven drying for 1 hour at 70 ^{o}C.

Characterization of biosorbents

The FTIR spectra of the biosorbents before and after adsorption of gold were obtained using ABB MB3600 spectrometer to characterize the resulting changes in the structure of the biosorbents. SEM analyses were done using JEOL JSM-5310.

Recovery of gold from the biosorbents

The oven dried biosorbents obtained from the biosorption process were initially incinerated using a blow torch. A pinch of sodium tetraborate was added in the resultant product and the incineration was continued. The residue was viewed under a microscope and photomicrographs were recorded.

RESULTS AND DISCUSSION

Development of biosorbents

The reaction between the ground mango peels and sulfuric acid resulted in the production of a black gel-like product (Figure 1) consistent with what was reported in the literature (Pangeni et al., 2012; Pangeni et al., 2012a). The results of the FTIR analysis of the biosorbents revealed that in general, acid treatment caused an increase in the intensity of peaks corresponding to different functional groups (Figure 2). Mango peel contains polysaccharides, aside from polyphenolic compounds (Ajila et al., 2008; Samonte & Trinidad, 2013), thus the increase in the intensity of the peak for C=O at about 1700 cm^{-1} due to acid treatment was expected. Pangeni et al. (2012b) also reported the appearance of a peak at around 1200 cm^{-1}, which was ascribed to be the C-O-C stretching. It is proposed that the peak at around 1040 cm^{-1} (Figure 2) may be attributed to the C-O-C stretching, which proves that cross-linking was successful.

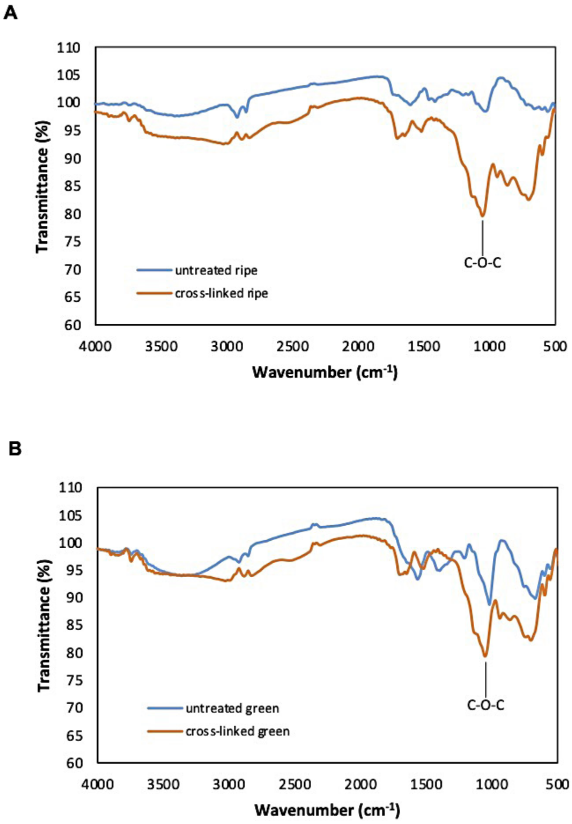

Figure 2. FTIR spectra of untreated and cross-linked (A) ripe and (B) green mango peel

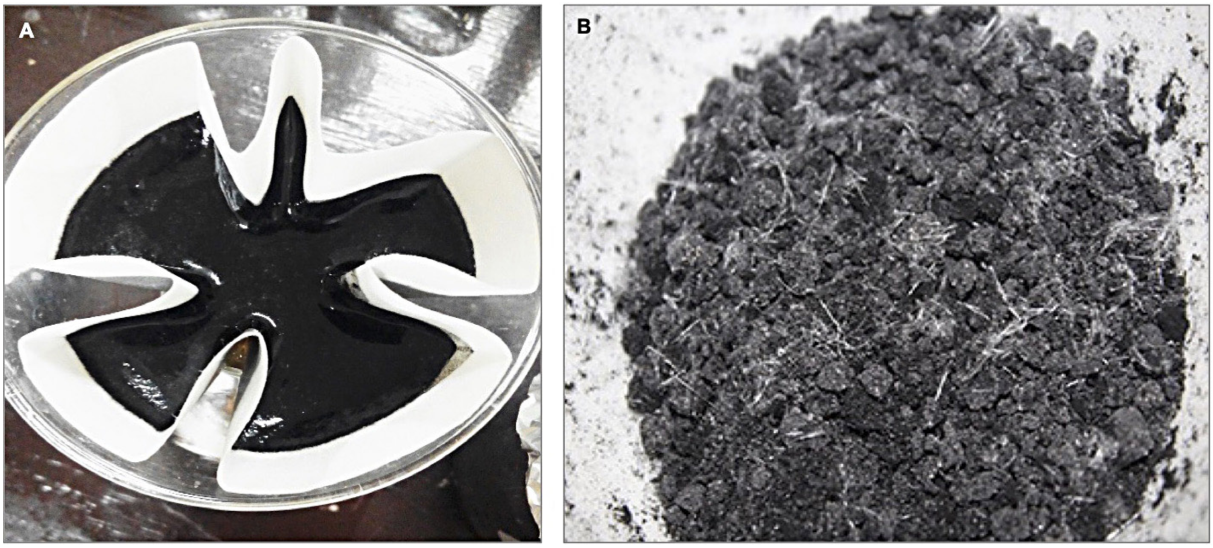

Figure 1. Gel-like substance (A) obtained after the reaction of mango peel and sulfuric acid and dried cross-linked biosorbent (B)

Biosorption of gold

Evidence of the reduction of gold ions by the cross-linked ripe (Figure 3A) and green (Figure 3B) mango peel biosorbents after 14 hours biosorption is investigated from the FTIR spectra. The increase in the intensity of the peak at around 1700 cm^{-1}, which corresponds to the C=O stretching, suggests the oxidation of the OH groups as a result of the reduction of gold ions to metallic gold. Similar results were previously reported for the biosorption of gold in polysaccharide (Pangeni et al., 2012) and tannin (polyphenols) gels (Inoue et al., 2015). The change in the intensity of the C=O peak, however, appears to be higher in the cross-linked green than in the cross-linked ripe mango peel, suggesting that the green mango peel biosorbents have better ability to reduce gold ions.

Two components of mango peel (polysaccharides and polyphenols) may be involved in the recovery of gold from the solution. The differences in the amounts of these substances in ripe and green mango peel may explain the variation in their ability to recover gold ions from solution. Polyphenols, anthocyanins and carotenoids are abundant in mango peel extract (Jahurul et al., 2015). However, the ripe and unripe mango peel extract have different concentration of polyphenols (Ajila et al., 2007). The major antioxidants in the peel extract of two mango varieties (Indian Raspuri and Badami) both ripe and unripe are the polyphenols. It was found out that the raw mango peel extracts for both varieties have a higher polyphenol content compared to the ripe mango peel extract. The effectiveness of the cross-linked green mango peels to recover gold from solution compared to the ripe mango can also be attributed to the changes associated with physiological development, including fruit ripening, seed germination, and cell wall expansion (Tharanathan et al., 2006). The polysaccharides contained in the cell wall of plants are being despoiled by the plants enzymes during the aforementioned developmental stages. During soft ripening of mangoes, changes occurring in the amount of polysaccharides are due to the pectin-degrading enzymes among cell wall hydrolases.

The use of mango peel powder, instead of the cross-linked gel, also led to the increase in the intensity of the peak for C=O in the FTIR spectra, suggesting that even raw mango peel

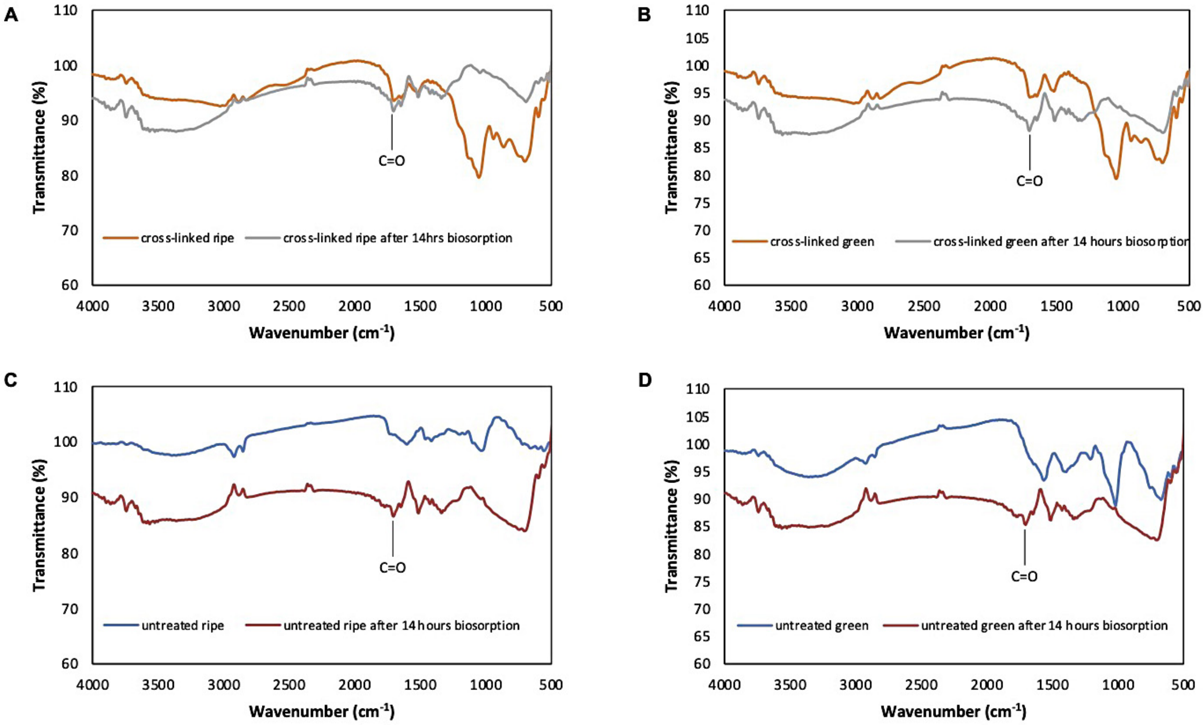

Figure 3. Sorption of gold on mango peel biosorbents. FTIR spectra of biosorbents before and after biosorption of gold: A and C – ripe mango peel; B and D – green mango peel; A and B – cross-linked mango peel; and C and D – untreated mango peel

can be used for the recovery of gold from a metal solution (Figure 3C and 3D). This is expected since there was a previous report on the use of dried and ground durian husk for the recovery of gold (Abidin et al., 2011). The surface of the crosslinked green biosorbent before and after gold biosorption was observed via SEM. The micrographs (Figure 4) show that the biosorbent has a smooth surface prior to gold sorption (Figure 4A). After the biosorption, particles adsorbed on the sample's surface are evident (Figure 4B). These observations are consistent with the findings of Shrestha (2016). The ability of the modified biosorbents to turn ionic gold to metallic gold was reported by (Fan et al., 2014) via the conversion of the trivalent gold to metallic form because of the redox reactions occurring in the process. The report is also consistent with the proposed mechanism (Rahmayanti et al., 2016) regarding gold adsorption on gallic acid-modified magnetite particles (Mag-GA). The mechanism involves the hydrogen bonding formation, reduction to metallic gold, and the concurrent oxidation of the hydroxyl groups of gallic acid. The redox reaction that took place in the process was illustrated by Ogata and Nakano (2005) as cited by Abidin et al. (2011). It involves the reduction of chlorogold complex to Au(0). The reduction of gold into metallic gold was also reported in the studies using modified cotton cellulose (Pangeni et al., 2012b), modified bagasse biosorbent (Rubcumintara, 2015) and persimmon peels (Fan et al., 2014).

Recovery of gold from the biosorbents

The gold-loaded biosorbents were incinerated to separate the gold from the biomass. Pangeni et al. (2012b) suggested incineration as one of the suitable alternatives to recover metallic gold from a gold loaded solution. When viewed under the microscope, metallic deposits obtained after incineration were apparent (Figure 5).

CONCLUSION

The untreated and cross-linked green and ripe mango peels were used to recover gold from e-waste. Successful cross-linking was indicated by the emergence of C-O-C stretching in the FTIR spectra. The evidence for biosorption of gold was the change in the intensity of the peak for C=O in the FTIR spectra, which represents the oxidation of the OH groups in the polysaccharide or polyphenol when gold ions turn to metallic gold. A more intense peak was observed in the cross-linked green mango peel than in the cross-linked ripe mango peel. Even the raw or untreated peels from ripe and green mangoes have the ability to recover gold. These results suggest that mango peel, an abundant agricultural by-product in countries like the Philippines, can be utilized in the selective recovery of gold from e-waste. The findings may serve as basis for the development of approaches that can simultaneously be applied in the management of agricultural and electronic wastes.

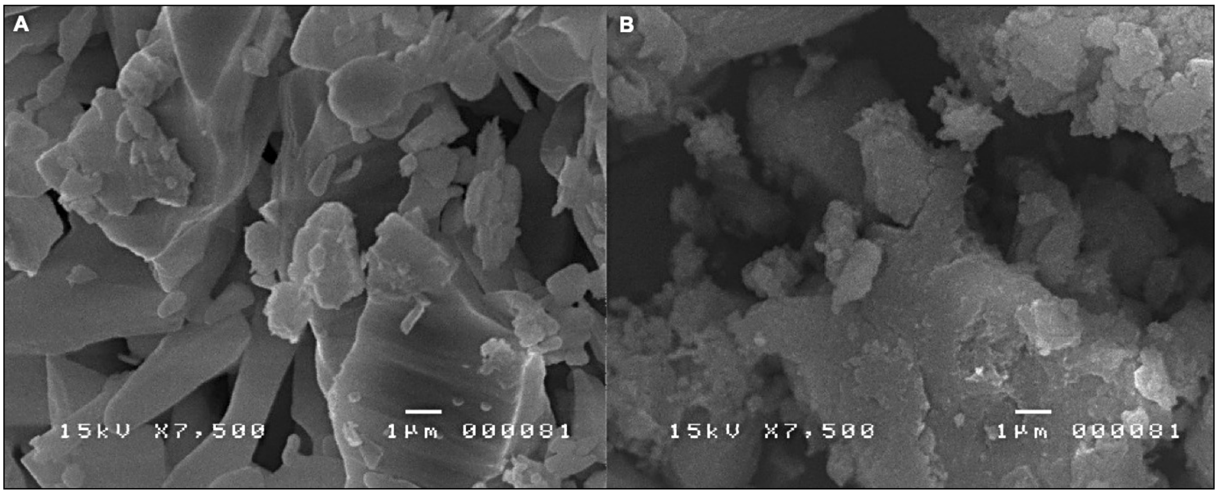

Figure 4. Scanning electron micrographs of cross-linked green mango peel before (A) and after (B) biosorption of gold

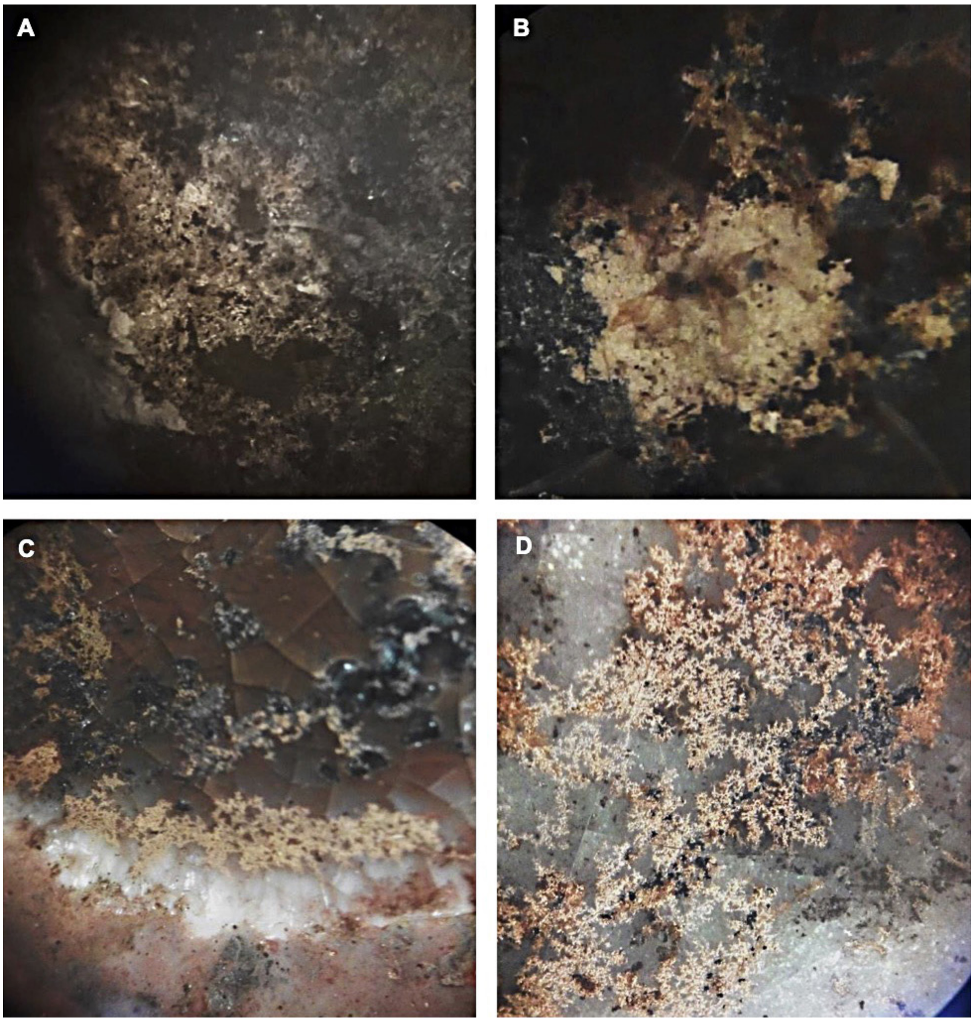

Figure 5. Photomicrographs of residue obtained after the incineration of gold-loaded biosorbents: untreated (A) and cross-inked (B) ripe mango peel; untreated (C) and cross-linked (D) green mango peel

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