Short Communication:

Study of Mangosteen Peel (*Garcinia mangostana* L.) Waste Capability to Recover Au(III) and Ag(I) in Aqueous Solution

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Abstract: *Electronic waste (e-waste) has been confirmed containing some precious metals such as gold and silver. Mangosteen peel waste as eco-friendly adsorbent has been studied to recover Au(III) and Ag(I) successfully. Recovery was started through adsorbent preparation, consisting of soxhlet extraction and maceration. About 100 mg of adsorbent was dispersed into Au(III) and Ag(I) solutions in various pH conditions (2–6). The result proves that the optimum adsorptions of Au(III) and Ag(I) are at pH 2 and pH 6, respectively. Au(III) adsorption follows the isotherm model of Langmuir with a maximum capacity of 0.580 mmol/g (114.27 mg/g). Ag(I) adsorption follows the isotherm model of Freundlich with a maximum capacity of 0.511 mmol/g (55.10 mg/g).*

Keywords: *mangosteen; recovery; Au(III); Ag(I); adsorption*

■ INTRODUCTION

Recovery of precious metals from secondary sources, such as e-waste, is considered more beneficial than mining them from primary sources [1-2]. The recovery process of precious metals, such as gold and silver, has been studied extensively. Precious metals are usually separated from e-wastes by leaching with a suitable solution before the recovery process begins [3]. Adsorption using bio-sorbent to recover precious metals is attractive due to its low-cost and eco-friendly [4-5]. The research of bio-sorbents for recovering Au(III) ions has been carried out, such as using a sulfur derivative of chitosan, dealginated seaweed waste, hen eggshell membrane, Ca-alginate beads [6], *Aspergillus niger,* and *Saccharomyces cerevisiae* [7], and also chitosan/SiO_2 coated on iron sand magnetic material [8]. Hydroxyl group of bio-sorbent active sites is responsible for the reduction of Au(III) to Au(0) and Ag(I) to Ag(0) [9-10].

The pericarp of mangosteen (*Garcinia mangostana* L.) is well-known as traditional medicine for inflammation, diarrhea, dysentery, etc., due to its high content of antioxidants [11-14]. Phenols and polyphenols are responsible for the antioxidant properties of mangosteen peel [15-16]. Phenolic compounds contained in mangosteen peel are tannins, flavonoids, xanthones, quinones, and vitamins [17-18]. The most abundant xanthone compounds found in mangosteen peel are α-mangostin, β-mangostin, and γ-mangostin [19-20].

Mangosteen peel has been investigated as bio-sorbent for its potential to adsorb metal ion in an aqueous solution. Zein and colleagues reported that unextracted mangosteen shell powder has a higher capacity than extracted powder for removal of heavy metal ions such as Pb(II), Cd(II), and Co(II) in aqueous solution [21]. Alkaline-saponified mangosteen pericarp exhibits more efficient adsorption capability than

unmodified mangosteen pericarp in adsorbing Cr(VI), Pb(II), Cd(II), Cu(II), Fe(III), Zn(II), and Ni(II) [22-23].

Herein, we conducted a study of mangosteen peel as an adsorbent to recover Au(III) and Ag(I) in an aqueous solution. The adsorbent was obtained from the solid residue of mangosteen peel extraction and characterized to study the active sites. Mangosteen peel as a biodegradable material containing the main active functional group as a form of a phenolic group (–OH) can interact with heavy metal ions such as Au(III) and Ag(I) effectively. Antioxidant compounds contained in mangosteen peel waste were investigated for binding and reducing Au(III) and Ag(I) in various pH conditions. Adsorption isotherm was evaluated by using Langmuir and Freundlich isotherm.

■ EXPERIMENTAL SECTION

Materials

Fresh mangosteen fruit was bought at a local market in Yogyakarta, Indonesia. The standard solution of Au(III) 1000 ppm was made by dissolving 1 g of pure gold (ANTAM) into 10 mL of aqua regia (a mixture of HCl (ACS Reagent 37%, Sigma-Aldrich) and HNO_3 (ACS Reagent 70%, Sigma-Aldrich) with a molar ratio of 3:1), followed by dilution using aqueous HCl solution 0.01 M until the volume reaching 1 L. The standard solution of Ag(I) was made by dissolving $AgNO_3$ (≥ 99% purity, Merck) into distilled water (Local Supplier). Methanol was obtained from Sigma-Aldrich with ≥ 99.6% purity.

Instrumentation

Functional groups contained in mangosteen peel waste were analyzed by using Shimadzu FTIR-8201 PC Fourier-transform infrared (FT-IR) spectrometer. The X-ray diffraction (XRD) method was performed by using Shimadzu XRD6000 with Cu-Kα. Analytik Jena contrAA300 atomic absorption spectrometer (AAS) was used to analyze the concentration of Au(III) and Ag(I).

Procedure

Adsorbent preparation

Fresh peel of mangosteen was dried in the open air under ambient conditions. The adsorbent preparation was begun by soxhlet extraction and followed by the maceration method under room temperature condition. The preparation method was a modification from our previous research [24]. Soxhlet extraction was performed by using methanol with a mass-to-volume ratio of 1 to 10. Methanol was used to extract the soluble organic substances in the mangosteen peel and to simulate the industrial process of extraction in order to obtain the mangosteen peel waste. The solid residue of mangosteen peel waste was separated by centrifugation. The maceration step was repeated until the liquid phase appeared colorless. The solid residue was dried under ambient condition and later applied as mangosteen peel waste (MPW) adsorbent. The adsorbent was characterized by using FT-IR spectrometer and X-ray diffractometer.

Adsorption experiments

The capability of MPW to recover Au(III) and Ag(I) ions was investigated by batch adsorption experiment. The adsorption experiment consisted of two parts, which were the determination of optimal pH condition and the adsorption isotherm. One hundred milligrams of MPW was dissolved into 100 mL of Au(III) and Ag(I) 100 mg/L solutions in various pH conditions (pH = 2, 3, 4, 5, and 6). The mixture was shaken briefly and left for 24 h. Subsequently, the mixture was heated at 60 °C for 30 min. The liquid phase was then separated by centrifugation, followed by Au(III) and Ag(I) analysis using an atomic absorption spectrometer. The same procedure was applied to determine the adsorption isotherm under the optimal pH condition. The initial concentrations of Au(III) and Ag(I) standard solutions were 40, 60, 100, 125, and 150 mg/L.

■ RESULTS AND DISCUSSION

Adsorbent Characterization

Preparation and FT-IR characterization of adsorbent

Maceration using distilled water after soxhlet extraction was conducted to remove water-soluble substances on the adsorbent surface. Without the maceration process, a colloid was formed during the adsorption experiment. The colloid was assumed to be the remaining active substance from mangosteen peel that dissolves in water. It interferes with the adsorption process.

FTIR characterization of mangosteen peel was shown in Fig. 1. Both dried mangosteen peel and MPW had two main functional groups at 3400 cm^{-1} and 1600 cm^{-1}, which correspond to the O–H and C=C aromatic stretching vibrations, respectively [24-25]. The absorption peak at 1280 cm^{-1}, associated with C–O stretching vibration [24], appeared to be deteriorated from fresh mangosteen peel after being treated. The extraction process removes organic and water-soluble compounds in fresh mangosteen peel. The hydroxyl group of polyphenolic compounds, which is considered as the active site, remained on the surface of the adsorbent, despite the extraction treatment. Other peaks did not appear to bear any significant difference between the two spectra, thus indicating that the method of adsorbent preparation did not damage the main structure of mangosteen peel.

X-ray diffraction characterization

Fig. 2 displays X-ray diffraction patterns of adsorbent before and after Au(III) adsorption. Based on trends given in Fig. 2, adsorbent with Au(III) was characterized by the XRD method due to its higher adsorbed percentage than Ag(I). In addition, both Au and Ag metals have similar cubical crystal system. MPW has an amorphous characteristic, showing no specific crystal pattern. On the contrary, adsorbent after Au(III) adsorption displays characteristic peaks at 34.35°, 38.28°, 44.47°, 64.72°, and 77.58°, which correspond to the reference pattern of gold metal (ICDD 00-004-0783). This proves that Au(III) ions were adsorbed and reduced to Au(0) metals on the surface of MPW. MPW has an irregular surface structure that was proven from stereo-microscope characterization on the previous research [24]. The presence of Au was not visible clearly due to the small amount of Au.

Optimal pH Condition of Au(III) and Ag(I) Adsorption

The ability of adsorbent to adsorb Au(III) and Ag(I) was proven by varying pH conditions of solution. Adsorption percentage of Au(III) and Ag(I) at various pH are presented in Fig. 3 with 3 times measurement using AAS. The optimum pH of Au(III) and Ag(I) adsorption were 2 and 6, respectively. Our previous research showed that the Point of Zero Charge (pH PZC) of mangosteen rind adsorbent was 3.7 [26]. Below the pH of PZC, the adsorbent tends to be positively charged and could interact electrostatically with $AuCl_4^-$ at pH = 2 condition. At pH = 2, Au(III) is negatively charged in the form of tetrachloroaurate(III) ions ($[AuCl_4]^-$), while the adsorbent surface is protonated and has a positively-charged surface. In an acidic solution, the possibility of electrostatic interaction between the functional group of adsorbent and $[AuCl_4]^-$ increases [26]. Ag(I) has a positive charge at a pH of 2–6.

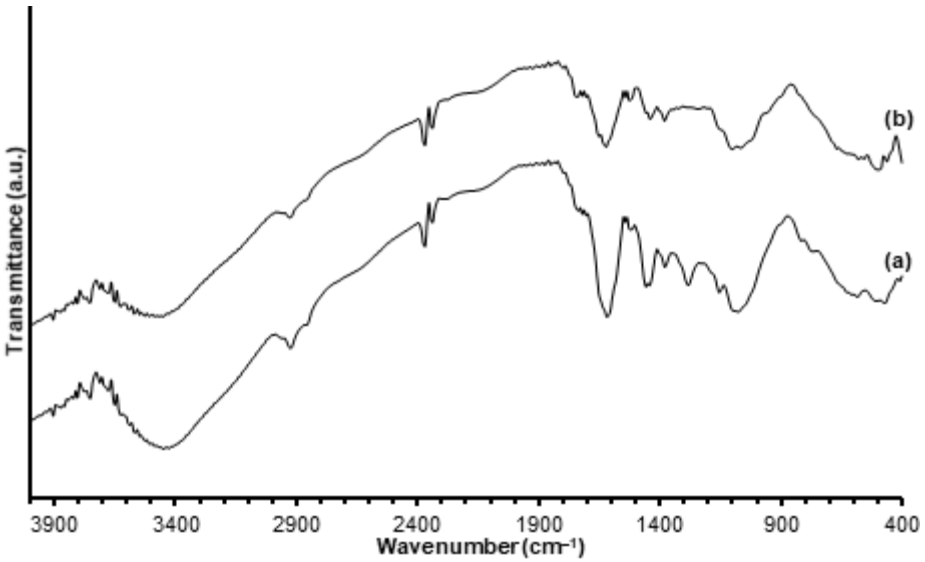

Fig 1. Infrared spectra of (a) dried mangosteen peel and (b) MPW

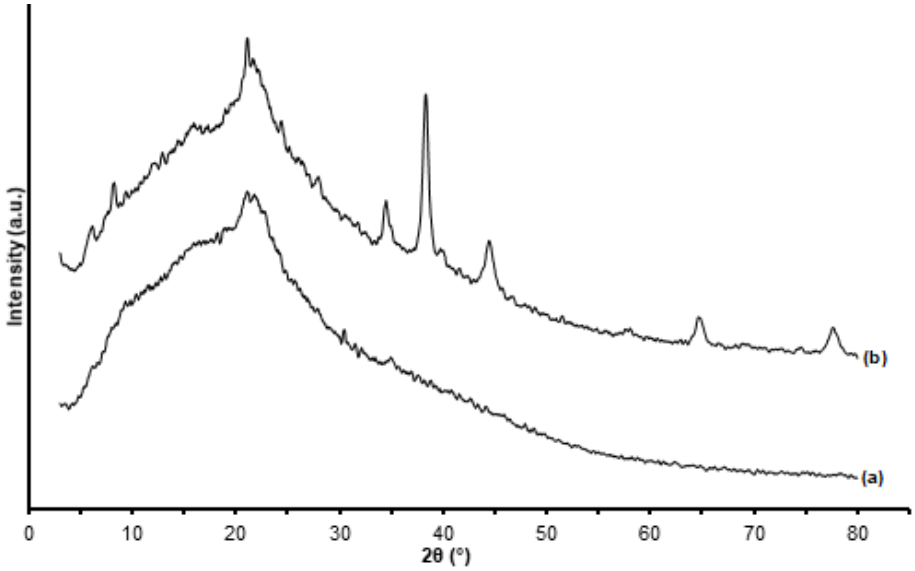

Fig 2. Diffraction patterns of MPW (a) before and (b) after Au(III) adsorption

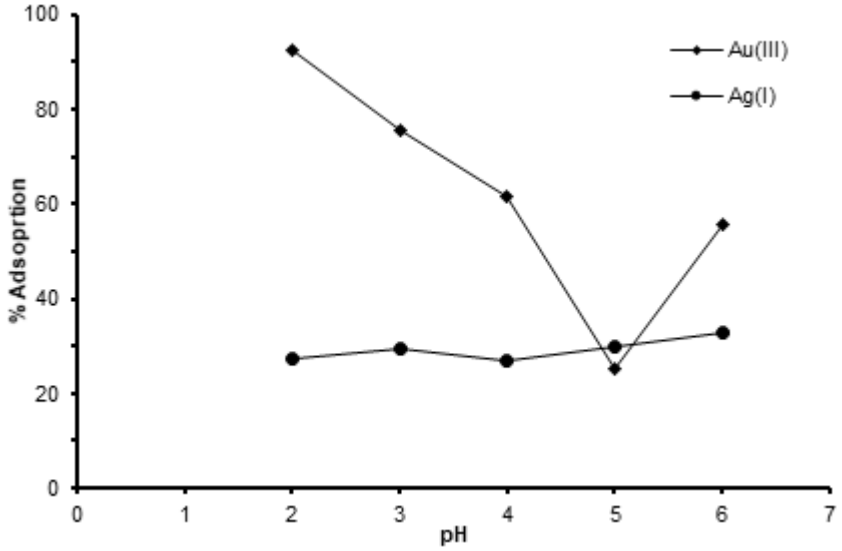

Fig 3. Trends of Au(III) and Ag(I) adsorption at various pH conditions

The optimum pH adsorption for Ag(I) was 6. At pH = 6 conditions, the adsorbent surface is deprotonated and formed a negative charge, thus promoting the interaction between Ag metal ions and the functional group of adsorbent surfaces electrostatically. The proposed adsorption mechanisms of Au(III) and Ag(I) on the surface MPW at their respective optimum pH condition are displayed in Fig. 4. Protonated phenolic groups bind with the negatively-charged $[AuCl_4]^-$ ions, while deprotonated phenolic groups bind with the positively-charged Ag(I) ions, electrostatically.

Adsorption Isotherm of Au(III) and Ag(I)

The adsorption isotherm pattern of adsorbed Au(III) and Ag(I) on mangosteen peel adsorbent were studied using various concentrations of Au(III) and Ag(I) solution. Fig. 5 presents the correlation curves between the adsorbed amount versus the initial concentration of Au(III) and Ag(I). Trends of the curves show that the amount of adsorbed Au(III) and Ag(I) increased with the increase of initial concentration. At respective optimum pH conditions, MPW could adsorb more Au(III) than Ag(I).

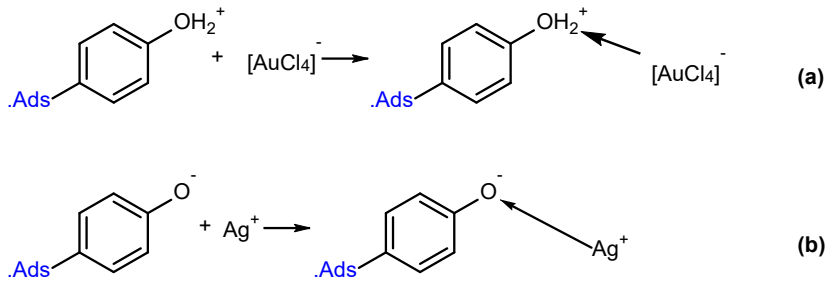

Fig 4. Proposed mechanisms of (a) Au and (b) Ag adsorption on MPW

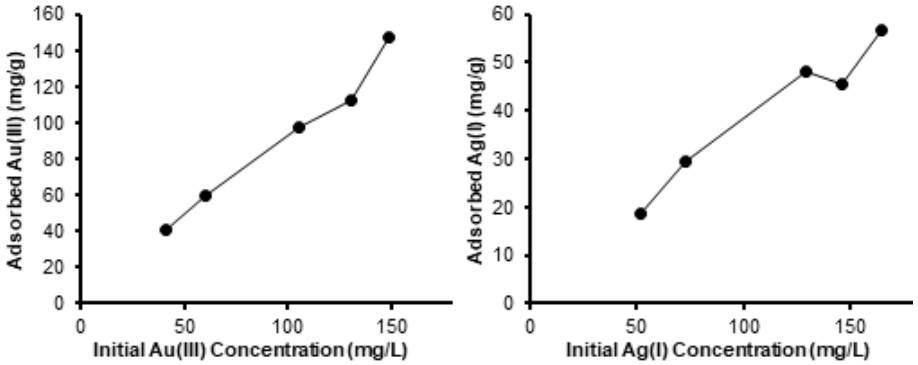

Fig 5. Correlation curves between adsorbed vs. initial amount of Au(III) and Ag(I)

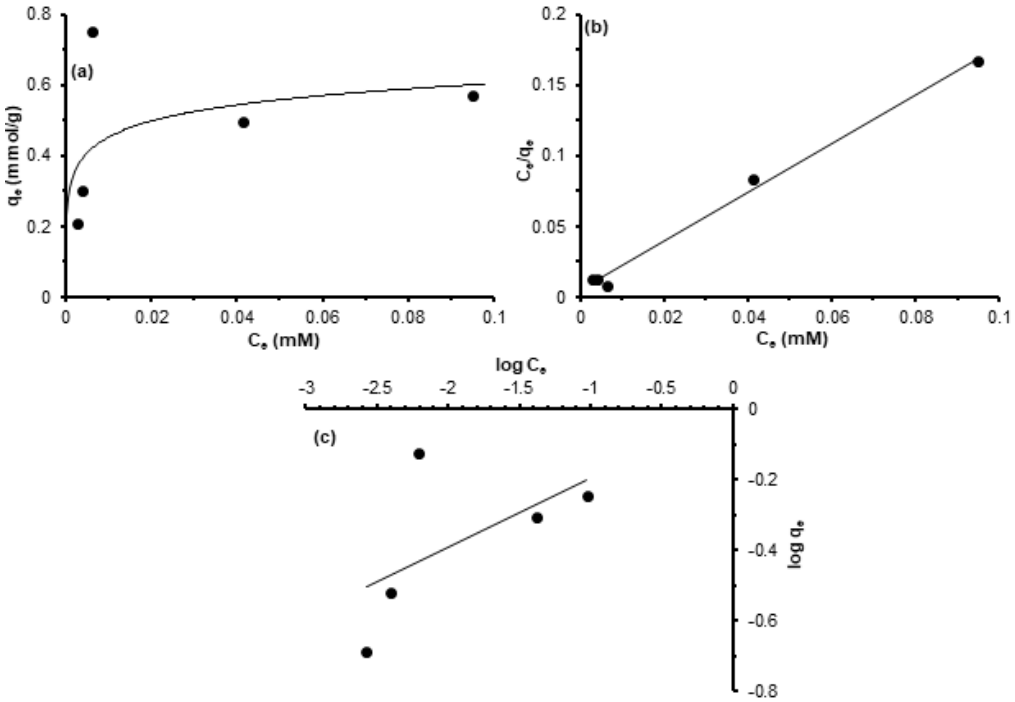

Fig 6. Adsorption plots of Au(III) on MPW according to (a) q_e vs C_e, (b) Langmuir, and (c) Freundlich models

Fig. 6 and 7 present the experimental plot of Au(III) and Ag(I) adsorption isotherm on MPW under optimum pH condition, together with Langmuir and Freundlich plot models. Langmuir plot was obtained by plotting C_e/q_e vs. C_e. It is based on the linear equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b.q_m} \quad (1)$$

where C_e is the equilibrium concentration of remaining

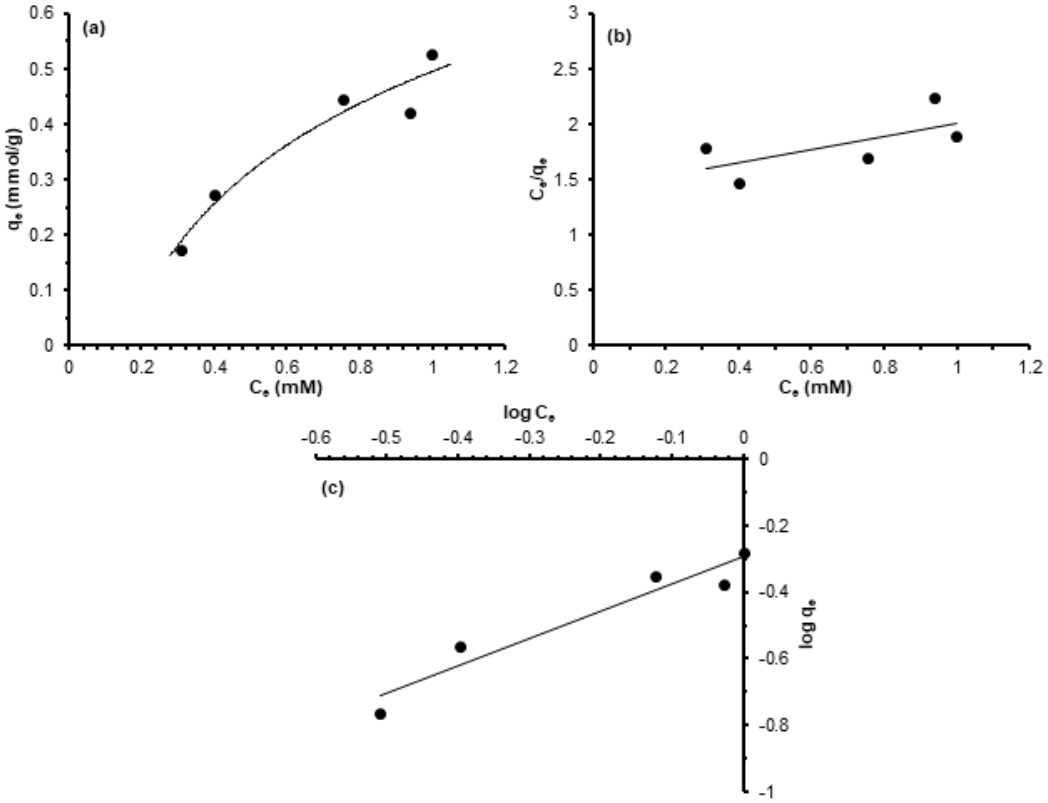

Fig 7. Adsorption plots of Ag(I) on MPW according to (a) q_e vs C_e, (b) Langmuir, and (c) Freundlich models

Table 1. Adsorption isotherm parameters of Au(III) and Ag(I) on MPW

	Langmuir			Freundlich		
	b (L/mol)	q_m (mmol/g)	R^2	K_f (mmol/g)	N	R^2
Au(III)	315.435	0.580	0.994	0.994	5.132	0.344
Ag(I)	0.418	1.690	0.429	0.511	1.212	0.926

adsorbate in the solution after adsorption (mM), q_e is the amount of adsorbed ions per unit weight of the adsorbent (mmol/g), q_m is the maximum amount of adsorbed ions per unit weight of the adsorbent (mmol/g), and b is Langmuir constant, which related to the energy of adsorption (L/mol) [2,27]. Freundlich plot was obtained by plotting log q_e vs. log C_e. It is based on the empirical linear equation:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (2)$$

where K_f is the Freundlich isotherm constant which approximates to adsorption capacity (mmol/g), and 1/n is a function of the strength of the adsorption [2,27]. Calculated parameters from the plotting of adsorption isotherm are presented in Table 1. Adsorption of Au(III) on MPW follows the Langmuir model, in which the R^2 value of the Langmuir plot is more proximate to 1 than the Freundlich plot. It can be concluded that each adsorbed Au(III) ions interacts with the active sites respectively and forms a monolayer on the surface of MPW. The calculated capacity of MPW to form a monolayer of Au(III) is 0.580 mmol/g or 114.27 mg/g. On the other hand, adsorption of Ag(I) on MPW tends to follow the Freundlich model, in which the R^2 value of Langmuir plot is less proximate to 1 than the Freundlich plot. It can be concluded that the adsorption of Ag(I) forms a multilayer on the surface of MPW. The calculated capacity of MPW to adsorb Ag(I) was approximately 0.511 mmol/g or 55.10 mg/g. The calculated capacity of Au(III) adsorption on MPW is relatively higher than Ag(I) adsorption.

■ CONCLUSION

The present work highlights the ability of MPW as metal ions adsorbent to recover Au(III) and Ag(I). The solid extract of mangosteen peel exhibits hydroxyl groups that can interact with metal ions. The optimum conditions of Au(III) and Ag(I) adsorption are attained at pH conditions of 2 and 6, respectively. Adsorption of Au(III) on MPW at optimum pH fits with the Langmuir model, while adsorption of Ag(I) on MPW at optimum pH fits with the Freundlich model. Adsorbed Au(III) forms a monolayer on the surface, while adsorbed Ag(I) forms a multilayer. Maximum capacity of adsorption using MPW reaches 0.580 mmol/g (114.27 mg/g) for Au(III) and 0.511 mmol/g (55.10 mg/g) for Ag(I). Adsorbed Au(III) ions are successfully reduced into Au(0) metals. MPW has the potential to be utilized as an eco-friendly adsorbent for recovering precious metals, particularly Au and Ag.

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■ AUTHOR CONTRIBUTIONS

Mellia Harumi, Rian Kurniawan, Agustiwandina Saputri, Dian Hanna Saraswati, Meissha Ayu Ardini, and Sri Sudiono conceived, planned, and carried out the experiments. Mellia Harumi, Rian Kurniawan, and Sri Sudiono wrote the manuscript and contributed to the final manuscript.

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