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Strategies for recovery of copper and gold as single constituents or an alloy: Selective separation and adsorption-coupled incineration of the bulk metal-loaded adsorbents

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ABSTRACT

To recover useful metals from waste PCBs, environmentally friendly bioleaching has recently attracted attention. Accordingly, distinct protocols are required to adequately recover the bioleached metals. Herewith, we present strategies to separate and recover copper and gold from a bioleached solution of waste PCBs. Polyethylenimine-polyacrylic acid composite adsorbents (PPCAs) were screened from among different candidate adsorbents. By only adjusting the mixing ratio of PEI and PAA, it was possible to recover gold and copper as single constituents or an alloy. A two-step strategy was designed, leading to the successful separation of copper and gold, first through selective adsorption of copper and then by bulk adsorption of copper and gold. The experimental maximum equilibrium uptakes of copper by PPCA-2 and PPCA-7 were 667±0.06 and 587±0.16 mg g^{-1}, respectively. The pseudo-first- and pseudo-second-order models fitted the kinetic data of copper better than gold. Following incineration, the adsorbents were characterized for examining the crystallinity and atomic energy states of the metals. Consequently, XRF analysis revealed that the copper-gold alloy ash contained 96.7±0.40% Cu and 1.73±0.26% Au. This study would be helpful for future studies that would aim at the separation and recovery of metallic minerals from bioleachates.

1. Introduction

With the advent of innovation and technological advances in the 21st century, electrical and electronic equipment (EEE) manufacture and use have steadily increased. The repercussion of this steady human progress leads to the generation of e-wastes, the mismanagement of which constitutes environmental health hazards (Bas et al., 2013; Li et al., 2014). The manufacturing industries, mainly personal computers and mobile phones sectors, are alleged to produce the highest amounts of metal-laden e-wastes, as they consume more than 30% of the global annual mined metals (Tay et al., 2013). This projection corresponds to an equivalence of 10 g – 10 kg gold per ton of electronic scraps, as against only 0.5 – 13.5 g gold per ton of natural gold ore (Cui and Zhang, 2008; Pham and Ting, 2009). This also represents approximately 100 – 350 g copper per kilogram of PCB (Işıldar et al., 2016). It is further projected that by 2020 and beyond, e-wastes from discarded computers and mobile phones would increase by 200 – 500% and 7 – 18%, respectively, from their 2007 levels (Bas et al., 2013; Li et al., 2014). Thus, the surging affluence in society, combined with the short useful lifespans of these electric and electronic gadgets, present real resource scarcity and challenging environmental pollution issues that require urgent attention.

Heavy metals such as arsenic, lead, chromium, and mercury require treatments to reduce their toxic effects, whilst precious metals such as gold, platinum, palladium, rhodium, and industrial metals including copper, etc. must be recovered in efforts to provide economic driving forces for their recycling from the e-wastes (Cui and Zhang, 2008; Korte et al., 2000). Recycling of e-wastes is thus an important endeavor from both environmental and economic viewpoints. Conventional hydrometallurgical and pyrometallurgical processes for metal recovery from e-wastes tend to use a lot of strong acids, resulting in the generation of toxic wastewater and off-gas emissions (Bas et al., 2013; Tay et al., 2013). For example, the pyrometallurgical process involves incineration

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Nomenclature

Acronym	Definition
E-waste	Electrical and electronic equipment waste
PCB	Printed circuit board
PEI	Polyethylenimine
PAA	Polyacrylic acid
GA	Glutaraldehyde
PPCA	PEI-PAA composite adsorbent
OPAC	Orange peel activated carbon
PAF	PEI-alginate fiber
PBBF	PEI-modified bacterial biosorbent fiber
CG-PAN	*C. glutamicum*-polyacrylonitrile

and smelting in a furnace at high temperatures, making it energy-intensive and cost-incurring (Bas et al., 2013; Li et al., 2014; Tay et al., 2013). Moreover, the hydrometallurgical process employs chemical lixiviants such as aqua regia (mixture of HCl and HNO_3 in 3:1 ratio) and cyanide which are environmentally non-sustainable due to their extreme corrosivity and toxicity, respectively (Li et al., 2014; Tay et al., 2013). As a result, researchers have been committed to finding alternative cost-effective, environmentally benign, and sustainable methods of extraction. Consequently, biohydrometallurgical (bioleaching) processes, i.e., leaching using microbes such as bacteria and fungi, have been discovered and proved to be effective for the treatment of both high- and low-grade e-wastes (Bas et al., 2013; Tay et al., 2013). Qiu et al. (2020) reviewed and proposed a systematic, value-added, and green route to recover full metallic resources from waste PCBs (Qiu et al., 2020). Bioleaching was highlighted as the most recommended extraction option, particularly when heavy and precious metals are present. Bioleaching uses cyanogenic microorganisms to produce cyanide and *in situ* leaches out metals (Qiu et al., 2020; Yuan et al., 2019). Examples of cyanogenic bacteria include *Bacillus megaterium, Pseudomonas aeruginosa, Pseudomonas fluorescens*, and *Chromobacterium violaceum* (Brandl et al., 2008; Li et al., 2014). The simultaneous secretion and utilization of cyanide in the biohydrometallurgical process makes it environmentally benign and sustainable.

After bioleaching, further processing is required for full solid metal recovery. Some of the applied processes include electrochemical refining, chemical cementation, solvent extraction, advanced oxidation and adsorption using ion exchange resins, microbial biomass or other classes of adsorbents (Bilal et al., 2013; Park et al., 2018). Among them, adsorption is viewed as one of the most promising methods owing to its simplicity, high efficiency, cost-effectiveness, and vast availability of adsorbent materials (Bediako et al., 2016; Won, S. W. et al., 2013). The adsorption technology functions effectively even in instances where the metal concentrations in the waste streams are minutely low, by accumulating or concentrating the dispersed metal ions within a small solid matrix, a situation which is considered a drawback in most of the other methods (Bediako et al., 2016; Demirbas, 2008). Based on the above reasons, the aim of the present study was to apply the adsorption technique to retrieve the leached metals from the bioleachate of waste PCBs. Specifically, the study sought to evaluate (screen) different adsorbents, select the best candidate, and then design special protocols to separate and recover bioleached copper and gold.

Several adsorbents, including biosorbents, carbon- and polymer composite-based materials, were initially screened through pre-adsorption experiments. Based on the preliminary results (section 3.1), the adsorbent comprising PEI and PAA was selected and further developed. Here, a strategy was devised to selectively separate and recover the bioleached copper and gold as single constituents or an alloy via adsorption-coupled incineration techniques. To the best of our knowledge, this is the first study reporting such strategy and it is thus expected to lay down a foundational guide for future bioleaching studies that would be geared towards separation and recovery of bioleached metals from e-wastes.

2. Materials and methods

2.1. Materials and chemicals

Highly viscous branched PEI (average molecular weight: ~ 750,000) was purchased from Sigma-Aldrich Ltd., Korea. PAA with molecular weight of 4,000,000 was procured from Polysciences (Asia-Pacific, Inc., Korea). GA (25 wt. %) was used as a crosslinking reagent and secured from Junsei Chemical Co., Ltd., Japan. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) which were used for pH adjustments were purchased from Daejung Chemical & Metals Co., Ltd., Korea. The pH values of samples were measured using a pH-meter (TOADKK HM-30R, Japan). A five–significant figure electronic balance (Precisa EP 220A, Switzerland) was used for sample weighing, and deionized water (DW) was used throughout the study for washing and preparation of solutions.

2.2. Adsorbents screening and selection

The various adsorbents that were screened include PAF (Bediako et al., 2017), OPAC (Bediako and Yun, 2018), PBBF (Park et al., 2012), PPCA (Bediako et al., 2020a), and CG-PAN composite fibers (not published), which are all adsorbents developed from our research group. PAF was prepared by extruding a mixture of PEI and alginate into Ca^{2+} and GA mixed solution for simultaneous gelation and crosslinking (Bediako et al., 2017). OPAC was synthesized through KOH activation of pre-carbonized orange peels at approximately 536 °C (Bediako and Yun, 2018). PBBF was prepared by ejecting a mixture of chitosan and *C. glutamicum* into NaOH solution and grafting PEI onto the obtained fibers through GA crosslinking (Park et al., 2012). The PPCA was produced by neutralizing PEI and PAA dissolved in NaOH with HCl, and subsequent crosslinking using dilute GA solution (Bediako et al., 2020a). CG-PAN composite fibers were fabricated by first dissolving polyacrylonitrile (PAN) in dimethylformamide (DMF), adding *C. glutamicum* powder to the solution and then extruding the suspension through a spirennet nozzle into DW. All the adsorbents were thoroughly washed with double distilled water to get rid of all residual chemicals before use.

The adsorbents were screened through adsorption experiments under acidic (pH 3-4), neutral (pH 7-8), and alkaline (pH 9-10) conditions. The reason for the pH variations was to test which pH would be suitable for retrieving the dissolved metal ions from the bioleachates using the various adsorbents. The experiments were carried out in 50 mL plastic bottles (falcon tubes) with adsorbent doses of 0.08g in 20 mL bioleachates. The falcon tubes containing bioleachates and adsorbents were placed in a shaking incubator kept at a temperature of 25±2 °C and rotation speed of 120 rpm. The pH of each solution was adjusted by adding drops of 0.1 – 0.5 M HCl or NaOH. The total volumes of acid/base added were negligible and did not affect the final volume of solutions. After 24 h of vigorous shaking and intermittent checking, the adsorption experiments were terminated by separating the adsorbents via centrifugation and analyzing the residual solutions using inductively coupled plasma-atomic emission spectrometer (Thermo Scientific ICP, iCAP 7000 series, USA). The metal uptakes and adsorption efficiencies were calculated using the mass balance expressions in Eq. (1) and Eq. (2), respectively.

$$\text{Metaluptake, } q = \frac{(C_o - C_e)V}{M} \tag{1}$$

Metal uptake,

$$\text{Adsorption efficiency } (\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where C_o and C_e are the initial and equilibrium concentrations of copper or gold (mg L^{-1}), V is the volume (L) of bioleached solution, and M is dry mass of adsorbent (g). The sampling for the ICP analysis was done by pipetting each residual solution into a 10 mL falcon tube and diluted as appropriate. For Cu analysis, the samples were diluted 31 times, and for Au analysis, the samples were diluted 3 times. In both cases, the dilution was done with DW to give final concentrations that were within the detection limit of the ICP. The experiments were conducted in triplicates by weighing each adsorbent into three different falcon tubes and performing the adsorption tests simultaneously and independently. Thus, the results shown are average values. In the cases where the standard errors are relatives small (Standard Error $< 2\%$), they are not shown on the plots. In Fig. 1, the composition of the PPCA was 0.5:2 (PEI:PAA); however, to find the best PPCA composition that could selectively separate and recover copper and gold, the protocol for the preparation of the PPCA was adjusted by tuning the proportions of the PEI and PAA (Table 1 and Fig. S1).

2.3. *Bioleachate*

Bioleachate generated from bioleaching experiments using waste PCBs and spent solutions was used as the metal ions source. The bioleachate was collected from various microbial cultures with different waste PCBs. However, major original source was the waste PCBs purchased from KiHoe Trade, a metal recycling company in Korea. The waste PCBs were ground into powder by an industrial hammer mill and then sieved. The grounded waste PCBs powder, with average particle size <850 μm, was used for the bioleaching experiments. The metal composition of the waste PCBs was in mg/g of Cu (445.62±2.35), Au (0.996±0.04), Fe (11.15±0.08), Ni (9.892±0.30), Zn (0.43±0.09), Ag (2.85±0.03), Pd (0.076±0.04), Sn (12.21±0.36), etc. However, only Cu and Au were present in detectable quantities in the bioleachate. The microbial culture conditions (pH, temperature and so on) were different according to the purpose of each experiment. *Chromobacterium violaceum* (KCTC No. 2897) used as the microbial source was purchased from the Korean Collection for Type Cultures (South Korea). The bioleaching procedure is as follows: the *C. violaceum* was first cultured in YP media containing yeast extract (5.0 g L^{-1}), polypeptone (10.0 g L^{-1}), and $MgSO_4 \bullet 7H_2O$ (1.0 g L^{-1}). The waste PCBs were added to the culture medium containing microorganism at a dosage ranging from 5 to 20 g L^{-1}, and was incubated in a shaking incubator at 120 rpm. However, culture conditions like pH, temperature, and aeration were changed according to the purpose of the experiments. After bioleaching experiments, the spent media containing bioleached metals (bioleachates) were collected and used for the metal recovery experiments. Prior to the metal recovery experiments, the bioleachates were centrifuged to separate the suspending particulate solids. The pH of the bioleachate collected over several months was 9.05 ± 0.17, and the concentrations of Au and Cu were 26 and 745 mg L^{-1}, respectively.

2.4. *Preparation of the PPCAs*

The PPCAs were prepared by adjusting our earlier protocol (Bediako et al., 2020a). The adsorbents were fabricated in a facile process by homogeneously blending different compositions of PEI and PAA to form solid complexes via strong poly-electrostatic interactions. In brief, weighed amounts of PEI and PAA (section 3.2) were separately dissolved in 20 and 80 mL each of DW in 100 mL beakers, respectively. The PEI solution was added drop-wise into the PAA solution whiles stirring gently to obtain a homogeneous solid mixture. The PAA was varied at 0.1, 0.5 and 1 g, whiles the PEI was varied at 0.5, 2 and 4 g. These variations were combined with each other to produce a total of nine (9) different combinations and thus nine different types of PPCAs. A schematic of the formulation process is shown in the supplementary material, Fig. S1. The serial numbers (S/#) provided in Table 1 correspond with the different types of PPCAs. For example, PPCA-1 was made from 4 g PEI and 0.1 g PAA, and PPCA-9 was made from 0.5 g PEI and 1 g PAA. After freeze-drying for 24 h, the solid materials were crushed into granules with the aid of a laboratory mortar, each dispersed in 30 mL of ~1% v/v GA solution and crosslinked for 3 h. The crosslinked granular adsorbents were then separated under vacuum filtration and freeze-dried again for 24 h to obtain constant weights.

Table 1
Notation and compositions of the PEI and PAA in the PPCAs

S/#	PEI (g) in 20 mL DW	PAA (g) in 80 mL DW
1	4	0.1
2	0.5	0.5
3	4	1
4	2	0.1
5	2	0.5
6	2	1
7	0.5	0.1
8	4	0.5
9	0.5	1

2.5. *Metal adsorption studies*

The adsorption experiments including pH, adsorption isotherms and adsorption kinetics were conducted in batch modes. Similar to the adsorbent screening experiments, these experiments were carried out in triplicates using 50 mL plastic bottles (falcon tubes). Firstly, the adsorption experiment for evaluating the 9 PPCA types were performed at pH 5.24±0.06 and pH 9.05±0.17 using adsorbent doses of 0.08g in 20 mL bioleachates. The falcon tubes containing bioleachates and adsorbents were placed in a shaking incubator maintained at a temperature of 25 °C and rotation speed of 120 rpm for 24 h. The adsorption isotherm and kinetics experiments were carried out at the natural pH of pH 9.05 ±0.17. The adsorption isotherms were conducted by varying the adsorbent doses from 0.01 – 0.3 g per 20 mL of bioleachates, and the contents were also placed in a shaking incubator at 25±2 °C and 120 rpm for 24 h. The adsorption kinetics experiments were performed in a relatively large volume of 100 mL and fixed adsorbent dose of 0.4 g. The experiments were carried out on a magnetic stirring equipment with bars rotating at 300 rpm. At predetermined time intervals up to 48 h, 1 mL of the bioleached solution was sampled from the bulk phase, centrifuged and diluted for analysis of residual metal ion concentration.

The samples were analyzed using the ICP and the metal uptakes and adsorption efficiencies were determined from Eq. (1) and Eq. (2), respectively. Consequently, the adsorption kinetics data were fitted through the pseudo-first- and pseudo-second-order kinetic models as shown in Eq. (3) and (4), respectively (Ho and McKay, 1999; Lagergren, 1898; Wei et al., 2016).

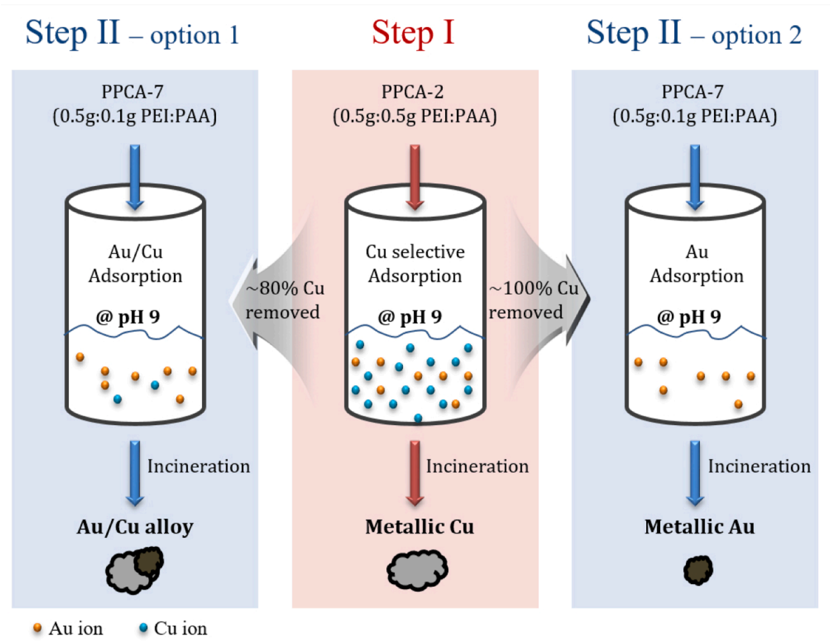
$$q_t = q_{e1}(1 - exp(-k_1 t)) \tag{3}$$

$$q_t = \frac{q_{e2}^2 k_2 t}{1 + q_{e2} k_2 t} \tag{4}$$

where q_{e1} and q_{e2} are the amounts of metal ions adsorbed at equilibrium (mg g^{-1}), q_t is the amount adsorbed at time, t (mg g^{-1}), k_1 is the first-order equilibrium rate constant (min^{-1}), and k_2 is the second-order equilibrium rate constant (g mg^{-1} min^{-1}). The kinetic data were first plotted using SigmaPlot software (version 12.0, SPSS, USA) and then regressed through the user-defined kinetic equations.

2.6. *Strategies for separating and recovering copper and gold*

A new strategy was designed to help separate and recover copper and gold as single constituents or an alloy (Scheme 1). As discussed later in sections 3.2 and 3.3, in the experiments examining the adsorption efficiencies of the 9 different PPCA types, PPCA-2 recorded approximately



Scheme 1. Strategies for recovery of copper and gold as single constituents or an alloy

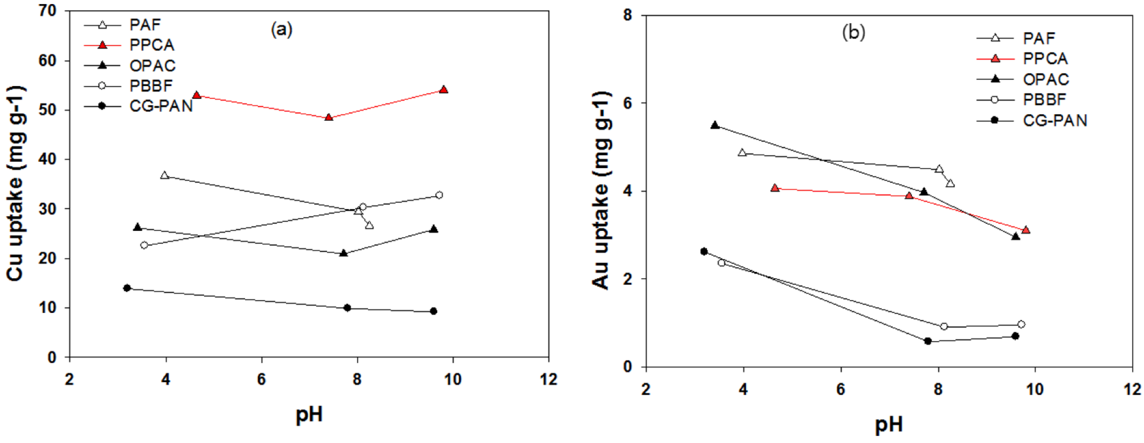


Fig. 1. Uptakes of (a) Copper and (b) gold by the various adsorbents screened. Experimental conditions: concentration = Au: 26 mg L^{-1}, Cu: 745 mg L^{-1}, adsorbent dose = 0.08g per 20 mL, pH = 3 – 10, temperature = 25±2 °C, reaction time = 24 h, Standard Error < 2%.

80% adsorption efficiency of copper, without gold adsorption, indicating remarkable copper selectivity. The adsorbent dose used for this experiment was 0.08g adsorbent per 20 mL bioleachate (4g L^{-1}). To increase the selective adsorption efficiency of copper, the adsorbent dose was increased up to 4 folds, i.e., 0.32 g adsorbent per 20 mL bioleachate (16 g L^{-1}), with all other adsorption conditions maintained as before. The aim was to reach 100% copper adsorption efficiency with PPCA-2 so that only gold would be left in the residual solution, thereby promoting the complete separation of the two metals at a single adsorption step. This process constitutes step I in the design Scheme 1. In the case that step 1 is achieved, the process automatically proceeds to step II – option 2, where only gold is present in the bioleachate and can be recovered using PPCA-7. However, in the case that step I is not achieved, the process proceeds to step II – option 1, where both copper and gold are present in the bioleachate and can be recovered as an alloy using PPCA-7. The PPCA-7 was selected for this step because it recorded almost an even adsorption efficiency of 55% for both copper and gold (Fig. 2). The adsorbent dose for this step is kept at 0.08 g adsorbent per 20 mL bioleachate. All the adsorption experiments were conducted at 25 ±2 °C and 120 rpm for 24 h, and each experiment was independently conducted three times (triplicated).

2.7. Incineration of adsorbent after adsorption

Adsorption-coupled incineration techniques involving initial selective copper adsorption or bulk adsorption of copper and gold, and subsequent incineration of the loaded adsorbents were undertaken to obtain single constituents or an alloy of the two metals. Incineration of adsorbents after adsorption is a good approach for recovering metals in their solid forms (Bediako et al., 2020b). Following adsorption of copper and gold using the PPCA-7, the adsorbent containing metals was filtered and dried overnight in a hot oven dryer at 70°C. The dried adsorbent was then placed in an automated furnace and incinerated at 400 °C in the presence of oxygen for 1 h to obtain metal-containing ashes. The incineration process was commenced by heating the sample at a heating rate of 20 °C min^{-1} starting from room temperature until the desired temperature of 400 °C was reached, and then held for 1 h. About 10 mg each of the burnt metal ashes were place in X-ray fluorescence equipment (XRF; M1 MISTRAL, Bruker, Germany) and analyzed for chemical composition.

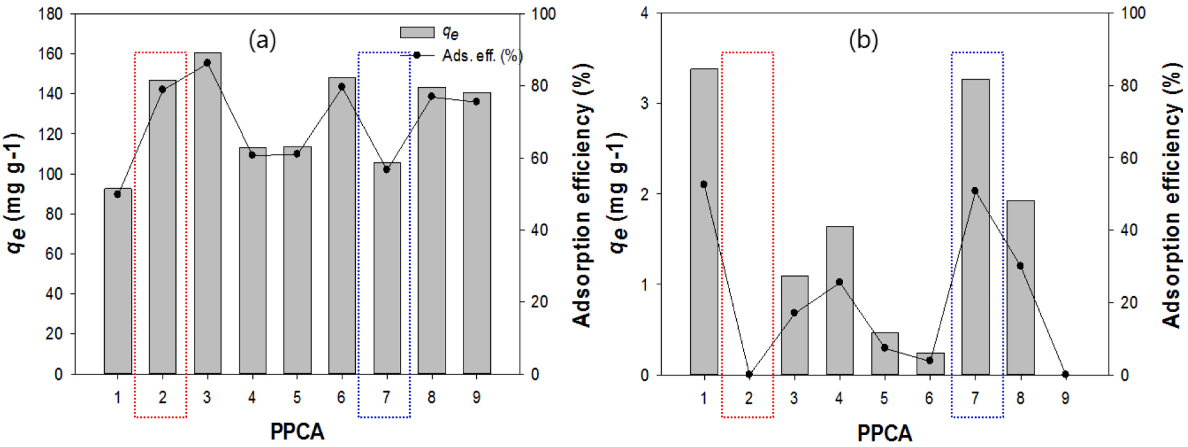


Fig. 2. Adsorption capacities and adsorption efficiencies of (a) copper and (b) gold by the PPCAs (numbers 1 – 9 defined in Table 1). Experimental conditions: concentration = Au: 26 mg L^{-1}, Cu: 745 mg L^{-1}, adsorbent dose = 0.08g per 20 mL, pH = 9.05±0.17, temperature = 25±2 °C, reaction time = 24 h, Standard Error < 2%.

2.8. *Instrumental information*

To understand the crystallinity, elemental states, and chemical interactions between the adsorbed metals and adsorbents, X–ray diffraction (XRD) patterns and X–ray photoelectron spectroscopy (XPS) spectra of the pristine adsorbents, i.e., before adsorption, and metal-loaded adsorbents, i.e., after incineration, were collected. Prior to XRD and XPS analysis, each adsorbent was prepared in the form of a fine powder using a mortar. The XRD patterns were collected with a Rigaku XRD operated with Cu-Kα radiation at 40 kV and 30 mA and processed using Jade 6 software. The Cu wavelength was 1.5406 Å, and the 2θ interval ranged from 5 to 90 degrees. The XRD profile was detected at 0.33 degrees for 69.85 seconds. For the XPS analysis, an AXIS-NOVA spectrometer (Kratos Analytical, Ltd., UK) with monochromatic Al K having a binding energy of 1486.71 eV photons as the X-ray source was used. The X-ray source was operated at a power of 180 W. During the XPS measurement, the pressure in the analysis chamber was maintained at less than 7×10^{-9} torr. X-ray fluorescence (XRF; M1 MISTRAL, Bruker, Germany) was used to quantitatively and qualitatively analyze the inorganic elements present in the metal-loaded ashes. The X-ray tube voltage and anode current were 50 kV and 800 μA, respectively.

3. Results and discussion

3.1. *Adsorbents screening*

The results of the adsorbent screening experiments are presented in Fig. 1 and Fig. S2. Except for the PBBF, the results showed interesting trends of generally low uptakes near neutral pH and high uptakes at acidic pH for both copper and gold, but high copper and low gold uptakes at alkaline pH. Overall, OPAC and the PEI-containing adsorbents, i.e., PAF and PPCA recorded higher adsorption efficiencies. This was likely because of the presence of doped-N groups in the OPAC matrix (Bediako, J. K. et al., 2020c), and the vast existence of primary, secondary and tertiary amine groups in the PEI (Song et al., 2017), coupled with the abundance of carboxyl ligands in the PAA and alginate polymers (Bediako et al., 2017; Park et al., 2018). The combined presence of cationic and anionic ligands meant that there were sufficient binding sites for both metal ions which likely existed as free species or cyanide complexes, according to previous studies (Choi et al., 2020; Isildar et al., 2016). Among the three best adsorbents, the order of adsorption efficiencies is approximately 60%, 40%, and 30% of copper and 70%, 85%, and 95% of gold for the PPCA, PAF, and OPAC, respectively (Fig. S2). Although the PAF and OPAC showed relatively higher gold uptakes, the PPCA was eventually selected for the subsequent studies owing to its higher uptake of copper, which is predominantly in large essence of gold in the bioleached solution.

3.2. *Evaluation of the PPCAs*

The 9 different PPCAs were evaluated at the bioleachate natural pH of pH 9.05±0.17, as well as pH 5.24±0.06. The metal uptakes and corresponding adsorption efficiencies are shown in Fig. 2 and Fig. S3, respectively. Copper adsorption efficiencies were comparably better under both pH conditions for all the different PPCAs prepared at different polymer ratios. However, there were huge fluctuations in the gold uptakes. At pH 5.24±0.06, PPCA-2, i.e., the PPCA containing 0.5 g:0.5 g PEI:PAA showed some level of selectivity towards copper, however, the efficiency was relatively low (Fig. S3). Alternatively, at pH 9.05±0.17, both PPCA-2 and PPCA-9, i.e., PPCA containing 0.5 g:1 g PEI:PAA, showed complete copper selectivity by capturing only copper without gold (Fig. 2). The mechanism behind this selective adsorption behavior was not fully understood, however, it is likely that the negatively-charged carboxyl groups of PAA were completely neutralized by the abundant amine groups of PEI via electrostatic interactions, and the remaining amine sites could coordinate the predominantly cationic copper ions via chelation (Bose et al., 2002). On the other hand, the PPCA comprising 0.5 g:0.1 g PEI:PAA (labeled PPCA-7) exhibited relatively identical affinities for both copper and gold, recording significantly high uptakes for both metals. Based on the above results, the new strategy was devised to recover the two metals as either single constituents via selective adsorption or as alloy mixtures through bulk scavenging.

3.3. *Separating and recovering copper and gold*

The strategy for obtaining copper and gold is summarized in Scheme 1. In the scheme, approximately 80% of Cu could be recovered in step I, and then step II-option 1 could be applied to recover the remaining Au and Cu as an alloy. Alternatively, when 100% of Cu is recovered in step I, step II-option 2 could be adopted to obtain pure Au. Thus, the first strategy was to selectively adsorb copper using PPCA-2 in step I, and then follow it with bulk adsorption of both Cu and Au using the PPCA-7 in step II – option 1. The 80% selective adsorption efficiency of Cu was obtained with 4 g L^{-1} adsorbent dose; it was therefore intuitive to think that by increasing the adsorbent dose, complete Cu recovery (100% adsorption efficiency) could be achieved. Contrary to this expectation, however, the adsorption efficiency only increased up to a peak value of

92% when the adsorbent dose was increased up to 16 g L^{-1} (4 folds). No further increase was observed beyond this value, suggesting that complete Cu recovery was unattainable with step I in the present scenario. This could be due to the limited affinity of the adsorbent to fully adsorb the Cu. To achieve complete Cu recovery using step I, the affinity of the adsorbent must be improved by introducing high-affinity functional groups such as thiol and sulfate/sulfonate groups (Cui and Zhang 2008; Bediako et al. 2020). Since step II – option 2 is dependent on the success of step I, it could not be realized due to the inability to fully achieve step I. Therefore, we adopted the strategies in step I (to recover only Cu) and step II – option 1 (to recover Cu and Au). With this, adsorbent characterization and further experiments were carried out as described under the methods.

3.4. Characterization of adsorbents before adsorption and after incineration

Previously, we characterized PEI and its composite with different polymers and biomasses (Bediako et al., 2020; Bediako et al., 2019; Song et al., 2017; Won et al., 2013). In this study, we zoom in on XRD and XPS analysis to understand the characteristics of the adsorbents and binding energy states of the attached metal complexes. The PPCA-2 and PPCA-7 were characterized before adsorption and after incineration. The XRD patterns of the adsorbents (before adsorption) showed backbone structural bumps at $2\theta = 21.8 – 26.6°$ (Fig. 3) (Bediako et al., 2017; Zhou et al., 2013). Before the incineration, no crystalline metal peaks were detected in both adsorbents PPCA-2 and PPCA-7. After incineration, the copper-selective PPCA-2 showed several peaks pertaining to copper diffractions. The two characteristic diffraction peaks at $2\theta = 35.5$ and 50.4° were indexed to 002 and 200 face centered cubic (fcc) lattices and represent cupric oxide, CuO (PDF#80-1917) and metallic copper (PDF#85-1326) (Chan and Teo, 2006; Khalid et al., 2015). The other diffraction peaks appearing at $2\theta = 38.7$, 38.9, 43.3, 48.6, 53.7, 58.3, 61.5, 66.2, 74.0, and 89.9° correspond to 111, 200, 111, -202, 020, 202, -113, -311, 220 and 311, respectively, indicating the mixed presence of cuprous oxide, Cu_2O and cupric oxide, CuO (Azam et al., 2012; Bediako et al., 2015). These suggest that oxygen present in the furnace is likely to react with copper to form copper oxide layers. On the other hand, the PPCA-7 exhibited diffraction peaks attributable to Au-Cu alloy (Dahal and Chikan, 2008). The 2θ angle values at 38.1, 38.6, 39.0, 44.2, 64.3, and 77.4° tallied well with reflections of the 111, 111, 200, 200, 220, and 311 fcc atomic planes of gold-copper alloy particles, respectively (PDF#04-0784 and PDF#80-0076) (Dahal and Chikan, 2008). Aside from the alloy peaks, fcc reflections corresponding to only copper and copper-related oxides appeared at $2\theta = 30.3$, 35.2, 48.9, 53.4, 61.4, 66.0, 67.8, and 75.1°. These did not portray phase segregation of the elements in the alloy particles, but rather due to the excess copper present in the ashes, which was as a result of its high initial concentration in the bioleachate.

For further study of the metal species, XPS core-level spectra of copper and gold were calved out of the survey spectra in Fig. S4 and deconvoluted into their respective elemental binding states. Fig. 4 depicts the spectra of the adsorbents before adsorption and after incineration. As evident from the graphs, the adsorbents (before adsorption) exhibited no traces of elemental peaks representative of the loaded metals, i.e., copper and gold. Meanwhile, the incineration of PPCA-2 yielded $Cu2p_{3/2}$ and $Cu2p_{1/2}$ peaks at 933.5 and 953.6 eV, with strong satellites at 942.5 and 962.5 eV, which correspond to copper oxides and copper metals, respectively (Fig. 4(a)) (Chen et al., 2015). However, there were no distinct gold peaks, which justified the copper-selective adsorption behavior of the adsorbent as observed from the adsorption experiments (Fig. 2). Conversely, the incinerated PPCA-7 displayed copper as well as gold peaks, an acknowledgement of the simultaneous adsorption of the two metals by the PPCA-7, and thus presence of copper-gold alloy in the burnt ashes (Fig. 4(b)). Whilst the copper ($Cu2p_{3/2}$ and $Cu2p_{1/2}$) peaks were at similar binding energy states as those of the PPCA-2, the emerged gold peak pair appeared at the binding energies of $Au4f_{7/2} = 84.3$ eV and $Au4f_{5/2} = 87.95$ eV, which represent metallic gold, Au(0) within the burnt ashes (Sylvestre et al., 2004; Xin et al., 2013).

3.5. Adsorption isotherms

The adsorption isotherm experiments were conducted to study the selective behavior and estimate the maximum equilibrium adsorption capacities of the selected PEI-PAA composite (PPCA) adsorbents. The selectivity of PPCA-2 towards copper was further manifested by the results shown in Fig. 5. It could be observed that in the bioleached metal mixture, the copper uptake increased gradually with the varying adsorbent doses (Fig. 5(a)), whilst the data points for gold adsorption clustered near the horizontal zero line (Fig. 5(b)). On the other hand, the PPCA-7 showed increasing uptakes for both copper and gold (Fig. 5(a) and (b)). However, in each case saturation could not be attained due to the steady rise of the data points. Largely, the adsorption capacity was found to be inversely related to the adsorbent dose, i.e., as the adsorbent doses decrease, the metal uptakes increase and vice versa. This

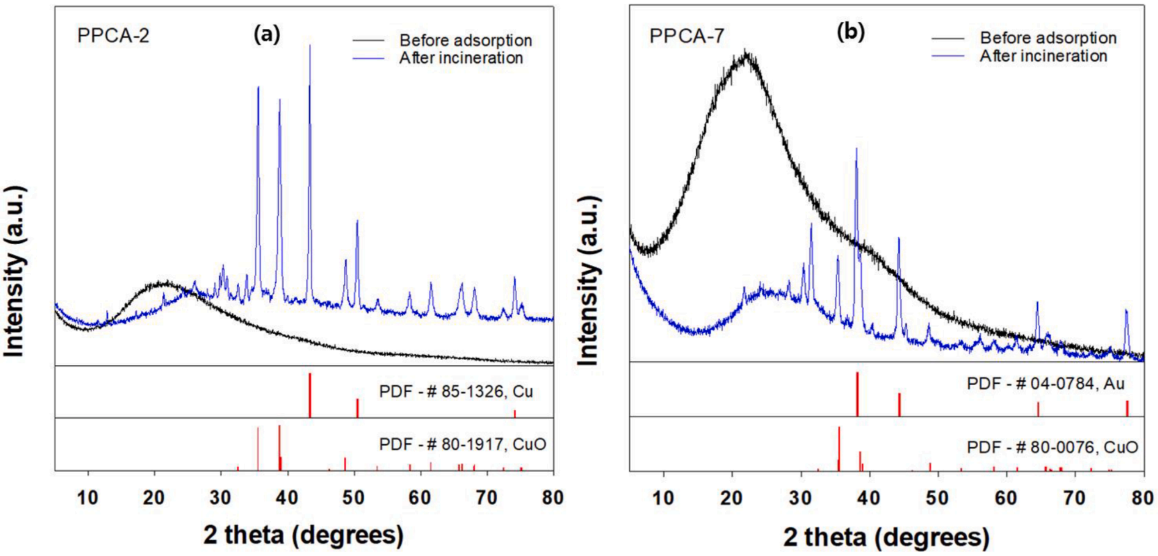


Fig. 3. XRD diffraction patterns of (a) PPCA-2 and (b) PPCA-7 processed using Jade 6 software.

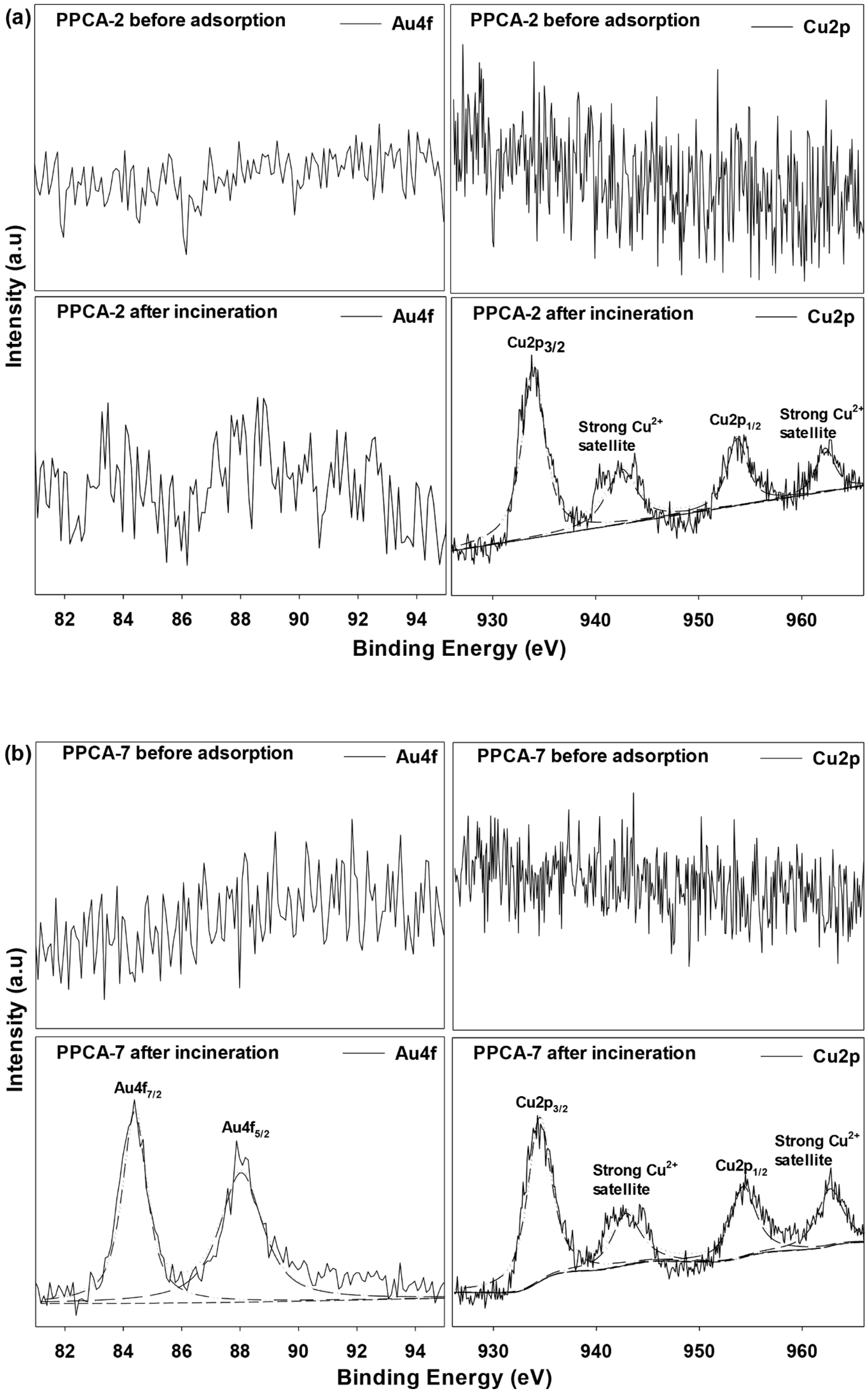


Fig. 4. XPS deconvoluted spectra of PPCA-2 and PPCA-7

phenomenon is fairly common in practical situations such as in the case of ruthenium recovery from industrial acetic acid waste solution using PEI-coated biomass-chitosan composite fiber (Kim et al., 2015). It could be explained first on the basis of affinity and then active binding sites. That is, the affinity of an adsorbent is characterized by initial sharp rising of the isotherm curve and a plateau-like top at equilibrium; however, this is not always true with natural systems which bear much complex compositions. At this point, the high adsorption capacities using lower adsorbent doses could be emphasized; however, increasing the adsorbent doses beyond certain limits could not improve the adsorption capacities proportionately. Consequently, the experimental maximum equilibrium copper uptakes reached 667±0.06 and 587±0.16 mg g^{-1} for PPCA-2 and PPCA-7, respectively. The experimental data could however, not adequately fit to any of the isotherm models examined due to the phenomenon described above.

3.6. *Adsorption kinetics*

The adsorption kinetics results are shown in Fig. 5 (c) and (d). Although the experiments were run for 48 h, equilibrium of each metal adsorption was attained within just 10 h, showing a relatively faster adsorption rate. Here again, copper selectivity was observed for PPCA-2, producing an equilibrium copper uptake of 157.55±10.07 mg g^{-1}, whiles that of PPCA-7 was 108.08±13.30 mg g^{-1}.

Having been fitted with the pseudo-first- and pseudo-second-order models, the kinetic regression data is shown in Table 2. The result

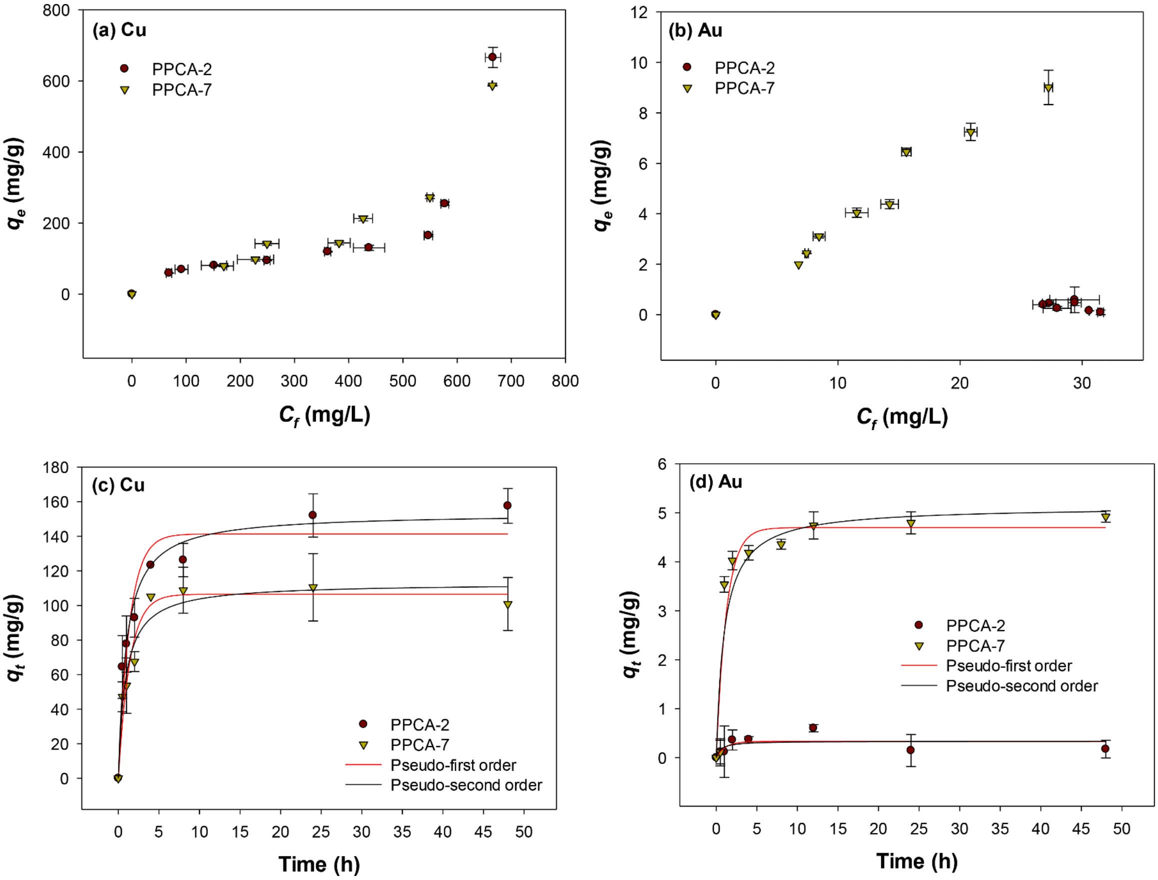


Fig. 5. Isotherm of (a) copper and (b) gold adsorption and kinetics of (c) copper and (d) gold using PPCA-2 and PPCA-7. Experimental conditions: concentration = Au: 26 mg L^{-1}, Cu: 745 and 149 mg L^{-1}, before and after adsorption using PPCA-2, respectively, adsorbent dose = Isotherm: 0.08g per 20 mL, kinetics: 0.4g per 100 mL, pH = pH 9.05±0.17, temperature = 25±2 °C, reaction time = 24 and 48 h for isotherm and kinetics experiments, respectively.

Table 2
Parameters estimated by the pseudo-first-order and pseudo-second-order models

Kinetic models	Parameters	Copper		Gold	
		PPCA-2	PPCA-7	PPCA-2	PPCA-7
Pseudo-first-order	q_1 (mg g^{-1})	141.35 ±8.33	106.51 ±4.92	0.33 ± 0.08	4.70 ± 0.32
	k_1 (min^{-1})	0.72 ±0.16	0.71 ±0.13	0.91 ±0.90	0.80 ±0.24
	R^2	0.9258	0.9550	0.4402	0.8905
Pseudo-second-order	q_2 (mg g^{-1})	153.42 ±5.78	112.91 ±6.09	0.34 ±0.10	5.13 ±0.46
	k_2 (g mg^{-1} min^{-1})	0.01 ±0.00	0.01 ±0.00	5.21 ±9.44	0.20 ±0.10
	R^2	0.9768	0.9531	0.3793	0.8701

suggests that for PPCA-7, both the pseudo-first- and pseudo-second-order models fitted the adsorption data with comparable R^2 values for both copper and gold. For the PPCA-2, the fittings for gold adsorption were very poor due to the less affinity of the adsorbent towards gold. With copper adsorption, the pseudo-second-order model produced a slightly better description of the data with a higher R^2 value. This likely resulted from the higher proportion of cationic amine groups in the PPCA-2, thereby leading to chemical complexation or chelation mechanisms (Bediako et al., 2019). The pseudo-second-order model suggests involvement of chemisorption mechanisms in the adsorption process (Boparai et al., 2011; Pillai et al., 2013). The model fittings for gold adsorption by PPCA-2 were however, not as good as compared to the copper adsorption. This was deemed due to the lower concentrations of gold in the bioleachate, coupled with the selectivity of the PPCA-2 towards copper rather than gold.

3.7. *Adsorption-incineration and recovery of metals*

Incineration involves a carbonization process in which the organic components are decomposed at relatively high temperatures and refined metals are consequently obtained (Bediako et al., 2020b). Not only does incineration have the advantage of recovering metallic elements but also recovers energy and reduces volume of waste (Gomes et al., 2020). Fig. S5 shows schematic images of the adsorption-incineration process and the obtained ashes containing copper and gold. The ash obtained after adsorption of Cu and Au using PPCA-7 was analyzed with XRF spectroscope. The result of the XRF analysis showed 96.7±0.40% Cu and 1.73±0.26% Au in the ash, along with negligible amounts of other base metals. It must be understood that the above metal composition is consistent with the concentrations in the bioleachate. Thus, given high Au concentration in the solution, alloys having much higher Au contents could be obtained.

4. Conclusions

This study has demonstrated the potential application of bioleaching-adsorption coupled incineration to recover precious and industrial metals from secondary resources such as waste PCBs. After the initial adsorbent screening using PPCA, PAF, OPAC, PBBF, and CG-PAN composite fibers, the PPCA exhibited remarkable performance and was utilized for the succeeding studies. By only adjusting the ratio of PEI and PAA, the PPCAs were capable of selective adsorption of Cu or both Cu and Au. Through adsorption isotherm experiments, the uptakes were found to be inversely related to the adsorbent doses, a case that led to steady rise of the isotherm data points and hence the inability to reach plateau-like equilibrium. This behavior is typical of natural wastewater systems with more compositional complexities than simulated solutions. Through the proposed two-step strategy, copper- and gold-containing ashes were obtained via selective adsorption using the PPCA-2 and bulk adsorption using the PPCA-7, after incineration in an automated furnace. It must be noted that this study has laid down a good strategy to recover metals from bioleached solutions; however, large volumes of the bioleachate and more adsorbents must be available in order to obtain more appreciable refined metals from the incinerated ashes.

CRediT authorship contribution statement

John Kwame Bediako: Methodology, Writing – original draft. **Jong-Won Choi:** Data curation. **Myung-Hee Song:** Software, Supervision. **Yeoung-Sang Yun:** Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2022.106264.

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