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# Adsorption of gold(III) on ionic imprinted amino-silica hybrid prepared from rice hull ash\*

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*Abstract*: In this research, the adsorption of Au(III) ion on ionic imprinted amino-silica hybrid (Im-ASH) in aqueous solution has been studied. Im-ASH was synthesized via sol-gel technique using a solution of sodium silicate  $(Na_2SiO_3)$  from rice hull ash (RHA) as the precursor and Au(III) ion as the template. Adsorption was carried out in a batch system with variation of pH, contact time, and Au(III) ion concentration. The selectivity of adsorbent toward Au(III) was examined in the presence of Cu(II) ion. The result of the kinetic study demonstrated that the adsorption of Au(III) ion followed pseudo-second order. The optimum adsorption of Au(III) on Im-ASH and non-Im-ASH was obtained at pH of 3.0. Im-ASH was twice as selective toward Au(III) ion than ASH was.

Keywords: adsorption; gold; imprinting; rice; silica.

# INTRODUCTION

Gold (Au) belongs to a precious metal group having many special characters and high economic value. It has various application ranges such as for jewelry, catalyst [1], and anticancer agent [2]. The increasing of demand and the decreasing of deposit has forced us to recover Au from secondary sources such as electronic and mining waste. Low concentration of Au ions and the presence of matrix ions in samples lead to inaccuracy in analyses, and hence a selective and sensitive method of analysis for Au(III) ion is required. To improve sensitivity and selectivity of the method, several techniques such as membrane filtration [3], liquid–liquid extraction [4,5], ion exchange (IE) [6], and solid-phase extraction (SPE) [7] have been used as an initial step of preconcentration and separation of Au(III) ions from matrixes before measurement with conventional analysis instruments. Among those techniques, IE and SPE are still being developed to find new effective and selective adsorbents for the target metal ions.

Several studies to obtain effective adsorbents have been undertaken by modifying silica to adsorb and preconcentrate trace-metal ions [8,9]. The results showed increasing adsorption capacity of transition-metal ion without being followed by increasing adsorption capacity of alkali and earth alkali metal ions. However, lower selectivity among the transition-metal ion group occurs. Ionic imprinting during polymer formation is a relatively new and potential technique to produce selective adsorbent. In this technique, the selectivity of adsorbent toward certain metal ions can be achieved because during the formation of adsorbent, the given metal ion plays a role as a template. Releasing the template ion from the

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polymer causes ionic imprinting polymer arrangement to be selective upon the template ion from other components in samples [10,11].

Ionic imprinting is originated from a molecular imprinting method that has been widely used in pharmaceutics [12] and biochemical separations [13]. The preparation of imprinted polymer through the molecular imprinting method involves three basic steps: (i) the monomers or oligomers form a complex with the template molecule; (ii) copolymerization between monomers (or oligomers)-template molecule complex with the cross-linker agent; and (iii) removal of the template molecule and resulting polymer, which has "memory" to recognize and to bind molecule template as its target [14]. This molecular "memory" is primarily due to two synergistic effects: (i) shape- and size-specific cavities that match the template molecule and (ii) functional group in polymer oriented to form multiple noncovalent complexation points with the molecule template [15]. Basically, the ionic imprinting structure method on silica is similar to the molecular imprinting method, but the ionic imprinting method uses metal ion instead of molecule as a template [16]. Metal ion will be removed from the silica structure and the resulting cavities with specific size and shape in the structure, and the resulting material is expected to be selective for the target metal ion.

Rice hull is one of the solid agricultural wastes still used in limited applications such as for livestock feed and fuel in pottery industries [17]. Rice production in Indonesia has been increasing annually and in 2012 is predicted to reach more than 72 million tons [18]. Rice hull contains silica around 15–20 % in rice hull [19] and around 89.47–98 % in rice hull ash (RHA) [20–23]. Silica of rice hull is concentrated in protuberances and trichomes on either the outer or inner epidermis of the rice hull [24]. Compared to wood materials, rice hull is one of the heavier plant materials with density higher than 1.4 g/mL due to the presence of silica [25]. Thermogravimetric analysis of rice hull shows that significant thermal degradation occurs within temperature ranges of 230–380 °C (nitrogen) and 230–540 °C (air), which is primarily attributed to the decomposition of hemicellulose and cellulose content [26]. Other organic constituents in rice hull are lignin, D-xylose, L-arabinose, methylglucuronic acid, and D-galactose [27]. As an adsorbent, rice hull exhibits lower oil sorption than kapok fiber and sugarcane bagasse. Its sorption capacity for diesel oil is 2.6 g g<sup>-1</sup> [28]. Incorporation of RHA in cement paste and concrete increases compressive strength due to reduced porosity, Ca(OH)<sub>2</sub> content, and width of the interfacial zone between paste and aggregate [29].

The high silica content and the abundance make RHA to be a potential silica source for producing new silica-based materials including adsorbents for metal ions. In this present paper, we report the utilization of  $Na_2SiO_3$  solution produced from RHA for the synthesis of ionic imprinted amino-silica hybrid (Im-ASH) through a combination of ionic imprinting technique and sol-gel process. The synthesized material was then used as an adsorbent for Au(III) ion in aqueous solution. The adsorption kinetics of Au(III) and the selectivity toward Au(III) in the presence of Cu(II) ion are evaluated, as well.

#### **EXPERIMENTAL**

## Materials

The rice hull sample used as the silica source was collected from an agricultural area in Bantul, Yogyakarta, Indonesia. The sample was burnt in open air to produce RHA. The solution of Au(III) ion 5000 mg L<sup>-1</sup> for the imprinting process was prepared in our laboratory by dissolving Au in an aqua regia solution. Sodium hydroxide  $\geq$ 97 %, hydrochloric acid 37 %, 3-aminopropyltrimethoxysilane (APTMS)  $\geq$ 98 %, thiourea  $\geq$ 99 %, sodium chloride  $\geq$ 99.99 %, copper chloride di-hydrate 99 %, and Au(III) standard solution 990–1100 mg L<sup>-1</sup> in analytical reagent grade and purchased from Merck, Germany were used without prior treatment.

# Instruments

A Fourier transform infrared (FTIR) spectrophotometer (Shimadzu FTIR-Prestige 21), a scanning electron microscope (SEM)/energy-dispersive X-ray (EDX) spectroscopy (JEOL JSM-6360LA), and a N<sub>2</sub>-BET/BJH analyzer (Quantachrome Instruments) were used for characterization of the adsorbents. The concentration of metal ion in the solution was analyzed using an atomic absorption spectrophotometer (GBC AAS 932 AA). For the adsorption process, this research was completed with supporting apparatus such as an oven (Heraeus B5050), a mechanical shaker (Marius Instrumenten), a magnetic stirrer (Thermolyne Cimarec 2), a vacuum pump (Buchi Var-V 500), and a centrifuge set (Kokusan Ensiki Ltd. type H-107).

# Synthesis of sodium silicate solution as precursor

RHA was milled to pass through a sieve size of 200 mesh. The powder of RHA 20 g was dissolved with 160 mL of NaOH 4 M by boiling the mixture in a closed erlenmeyer flask for 90 min with constant stirring. The residue was heated at 500 °C for 30 min in a furnace. The gray solid product was soaked in 200 mL of demineralized water for 3 d, and the mixture was filtered using Whatman No. 42 filter paper. The filtrate containing  $Na_2SiO_3$  was used as a precursor in the adsorbent preparation.

## Synthesis and characterization of adsorbent

In this study, two kinds of adsorbents, ASH and Im-ASH, were synthesized via sol-gel process. In the preparation of Im-ASH, a mixture of 100 mL Na<sub>2</sub>SiO<sub>3</sub> solution produced from RHA, 10 mL APTMS, and 10 mL Au(III) solution 5000 mg L<sup>-1</sup> was added with 3 M HCl solution dropwise with constant stirring until pH reached 7. The resulting gel was aged for 3 d, washed with demineralized water, and dried in an oven at 70 °C for 2 h. The resulting dry gel was ground and sieved 200 mesh in size. The content of Au(III) in the dry gel was released using a leaching agent of thiourea-HCl solution. The ASH was synthesized through analogue steps without adding Au(III) solution (Fig. 1).



**Fig. 1** Influence of HCl concentration in thiourea-HCl solution on Au(III) leached (left) and cycle of leaching process (right) on Au(III) leached from Au(III)-ASH (adsorbent mass: 0.25 g, volume of thiourea-HCl solution: 10 mL, concentration of thiourea in thiourea-HCl solution: 7 %, leaching time: 1 h).

Two kinds of the adsorbents Im-ASH and ASH were characterized using an FTIR spectrophotometer to identify the presence of the functional groups, using SEM-EDX spectroscopy for examining the micrograph profile and the elemental composition and a  $N_2$ -BET/BJH instrument for analysis of the surface area, the pore volume, and the pore radii.

## Adsorption

Adsorption was carried out in a batch system by adding 50 mg of the adsorbent in 20 mL of  $CH_3COONa$ -HCl buffer solution containing Au(III) ion 50 mg L<sup>-1</sup> at various pHs (from 1 to 5). The mixture was stirred for 2 h and centrifuged at 2000 rpm for 30 min. The concentration of Au(III) ion in supernatant was analyzed with a flame atomic absorption spectrophotometer (FAAS). The amount of Au(III) ion adsorbed was calculated based on the FAAS data using eq. 1.

$$Q = (C_0 - C_e)V/W \tag{1}$$

where Q represents the amount of the metal ion adsorbed (mg g<sup>-1</sup>);  $C_0$  and  $C_e$  are the initial and the final concentration of the metal ions (mmol L<sup>-1</sup>), respectively; W is the mass of the adsorbent (g), and V is the volume of the metal ion solution (L).

An analogue work of the adsorption was carried out by varying contact time (from 10 to 150 min) at constant pH to study the kinetics of the adsorption. Several models of the kinetics (first order, second order, pseudo-first order, and pseudo-second order) were examined and the rate constants were calculated.

Additionally, adsorption in various concentrations of Au(III), in a range of 50–300 mg L<sup>-1</sup> at constant pH and contact time was conducted, as well. The resulting data were evaluated using Langmuir [30] and Freundlich [31] equations to calculate the adsorption capacity. The selectivity of the adsorbent in adsorbing Au(III) ion was evaluated in the presence of Cu(II) ions with different concentration. The selectivity coefficient and the relative selectivity coefficient were calculated using eq. 2.

$$D = Q/C_{\rm e}; k = D_{\rm Au}/D_{\rm Cu}; k' = k_{\rm i}/k_{\rm n}$$
<sup>(2)</sup>

where D represents distribution ratio,  $D_{Au}$  and  $D_{Cu}$  is distribution ratio of Au(III) and Cu(II), k is selectivity coefficient, k' is relative selectivity coefficient,  $k_i$  and  $k_n$  are selectivity coefficient for the imprinted and the non-imprinted adsorbent, respectively.

## **RESULTS AND DISCUSSION**

#### Characteristics of Im-ASH

#### Functional groups in adsorbents

To confirm the presence of amine groups from APTMS in the functionalized silica, the FTIR spectra of silica gel (SG), ASH, and Im-ASH were compared and expressed in Fig. 2. Bands observed at 3426, 1636, and 957 cm<sup>-1</sup> indicate vibration of O–H from silanol group (*Si–OH*), and at 1088 and 463 cm<sup>-1</sup> come from *Si–O–Si* vibration of the siloxane group. Characteristic spectra of ASH and Im-ASH are similar, in which bands of *N–H* at 1528 cm<sup>-1</sup> and of *C–H* at 2940 cm<sup>-1</sup> are observed.

Amine group  $(-NH_2)$  of APTMS is protonated to result ammonium group  $(-NH_3^+)$ . This ammonium group binds anion of Au(III) via electrostatic interaction. Gelation between Na<sub>2</sub>SiO<sub>3</sub> and protonated APTMS, which binds Au(III) ion, is initiated by H<sup>+</sup> from HCl. Na<sub>2</sub>SiO<sub>3</sub> and APTMS binding Au(III) are co-hydrolyzed and co-condensed to form siloxane bridges (*Si*–*O*–*Si*) during the process. In the end of gelation, hard ionic ASH is found. The bonded Au(III) in ionic ASH is removed using concentrated thiourea solution. Au(III) is unstable in thiourea solution and is reduced to form Au(I). Monovalent Au ion is binded by thiourea and it forms a stable complex based on reaction eq. 3 [32].

$$\operatorname{Au}^{+}(\operatorname{aq}) + 2 \operatorname{SC}(\operatorname{NH}_{2})_{2}(\operatorname{aq}) \rightleftharpoons \operatorname{Au}[\operatorname{SC}(\operatorname{NH}_{2})_{2}]_{2}^{+}(\operatorname{aq})$$

$$\tag{3}$$

Thiourea solution 7.0 % is able to leach Au(III) from Im-ASH only 17.6 %. In order to increase the amount of Au(III) to be leached, HCl was added in thiourea solution. H<sup>+</sup> from HCl stabilizes Au(III) as HAuCl<sub>4</sub> molecule. Because of neutral charge, electrostatic interaction between HAuCl<sub>4</sub> and ammonium group on silica structure tends to be weak. HCl can increase the amount of Au(III) leached up to 70.0 %. The leaching process using thiourea-HCl solution was done repeatedly to leach Au(III) ion

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Fig. 2 FTIR spectra of SG (A), ASH (B), and Im-ASH (C).

incorporated inside of ASH. Almost 100 % of bonded Au(III) ions can be removed after 4 times leaching processes. After all of the Au(III) ions are released, the ionic Im-ASH containing tailor-made cavities is produced.

# Porosity of adsorbents

The specific surface area, the pore volume, and the pore radii of Im-ASH, ASH, and SG are presented in Table 1. The Brunauer–Emmett–Teller (BET) surface area of Im-ASH is found to be 143.68 m<sup>2</sup> g<sup>-1</sup>. This value is higher than the surface area of SG and slightly higher than the surface area of ASH. The pore specific volume and the average pore radii of Im-ASH are also higher than that of SG and ASH. During the sol-gel process, silicic acid reacts with other silicic acids to result in a dense silica structure. Addition of aminopropyltrimethoxysilane molecules decreases the density of ASH in comparison to SG but increases the specific surface area of ASH. Removal of the template Au(III) ion from the SG leads to formation of porous structure of Im-ASH. Therefore, it can be understood that the specific surface area, the pore volume, and the average pore radii of Im-ASH are in general higher than those of SG and ASH.

Adsorbent	Surface area m <sup>2</sup> /g	Pore volume cc/g	Pore radii Å
SG	95.77	0.67	15.35
ASH	130.65	0.91	74.44
Im-ASH	143.68	1.04	157.52

**Table 1** BET-surface area and BJH-porosity of SG, ASH, andIm-ASH.

In order to know the surface morphological image, the synthesized Im-ASH, ASH, and SG were characterized using SEM. The SEM image was observed in order to know the effect of Au(III) imprinting on the ASH structure. As seen in Fig. 3, SG, Im-ASH, and ASH have irregular shapes. The EDX analysis was performed to identify the elemental composition of Im-ASH, ASH, and SG. The elemental compositions of Im-ASH, ASH, and SG are presented in Table 2. The presence of nitrogen in Im-ASH and ASH indicates that  $-NH_2$  is successfully attached in the silica structure.



Fig. 3 SEM images of SG (A), ASH (B) and Im-ASH (C).

Element	SG (%)	ASH (%)	Im-ASH (%)
C	5.36	14.79	13.08
Ν	_	6.56	8.02
0	50.40	41.89	42.02
Si	44.24	36.76	36.88

**Table 2** Elemental composition for SG, ASH, andIm-ASH.

# Adsorption of Au(III) on Im-ASH

# Effect of pH

The data of the amount of Au(III) adsorbed at various pHs is expressed in Fig. 4. The amount of Au(III) adsorbed on Im-ASH and ASH increases with the increasing pH. Point of zero charge (pzc) of the adsorbent can be used to explain the phenomenon of the Au(III) adsorption on Im-ASH and ASH. Primary amine groups ( $-NH_2$ ) of ASH has pzc of 10; therefore, in the solution with pH < 10 primary amine groups are protonated to form ammonium groups ( $-NH_3^+$ ) and this protonation occurs perfectly at pH < 5.7 [33]. At pH 1 to 2, the adsorption of Au(III) is interfered by the presence of Cl<sup>-</sup> ions. In this condition, competition between Cl<sup>-</sup> and Au(III) to bind ammonium group occurs in the surface of Im-ASH and ASH. Electrostatic interaction between Au(III) and ammonium group occur maximum at



**Fig. 4** Influence of solution pH on Au(III) adsorption onto ASH and Im-ASH (Au(III) initial concentration: 50 mg  $L^{-1}$ , adsorbent dose: 2.5 g  $L^{-1}$ , contact time: 120 min).



Fig. 5 Influence of contact time on Au(III) adsorption onto ASH and Im-ASH (Au(III) initial concentration: 50 mg  $L^{-1}$ , pH 3, adsorbent dose: 2.5 g  $L^{-1}$ ).

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pH 3, and at this pH, competition between Au(III) and Cl<sup>-</sup> ions is relatively lower in comparison to that at pH 1 to 2. Adsorption at pH 4 and 5 showed a similar result to that at pH 3. Adsorption of Au(III) ions in basic media pH > 5 was avoided in this research due to precipitation of Au(III) hydroxide [34]. As seen in Fig. 5, the optimum adsorption is at pH of 3. At this pH, neither precipitation of Au(III) nor Cl<sup>-</sup> competition is expected, and this condition was used for the next adsorption experiment.

#### Adsorption kinetic

The effect of the contact time on the Au(III) adsorption by Im-ASH and ASH is presented in Fig. 5. First order (eq. 4) [35], second order (eq. 5), pseudo-first order (eq. 6) [36], and pseudo-second order (eq. 7) [37] were applied to evaluate the experimental data.

$$\ln C_{\rm e} = -k_1 t + \ln C_0 \tag{4}$$

$$(1/C_{\rm e}) = k_2 t + (1/C_0) \tag{5}$$

$$\log (q_e - q_t) = \log q_e - (k_3/2303)t \tag{6}$$

$$(t/q_t) = (1/k_4 q_e^2) + (t/q_e)$$
<sup>(7)</sup>

where  $C_e$  is concentration of Au(III) at equilibrium (mmol mL<sup>-1</sup>),  $C_0$  is initial concentration of Au(III) (mmol mL<sup>-1</sup>);  $q_e$  and  $q_t$  are amount of Au(III) on the adsorbent at equilibrium (mmol g<sup>-1</sup>) and at any time t (mmol g<sup>-1</sup>), respectively;  $k_1, k_2, k_3$ , and  $k_4$  are adsorption rate constant of first order (min<sup>-1</sup>), second order (mM<sup>-1</sup> min<sup>-1</sup>), pseudo-first order (min<sup>-1</sup>), and pseudo-second order (mM<sup>-1</sup> min<sup>-1</sup>), respectively. The calculation of the adsorption rate constant and the linearity are shown in Table 3. The correlation coefficient,  $R^2$ , shows that adsorption fits to pseudo-second order model. This model usually occurs on reaction in a buffer system where the concentration of H<sup>+</sup> ion is assumed to be constant or in reactions wherein the concentration of one of the reagents is in excess condition and relatively constant during the reaction. The adsorption of Au(III) ions on Im-ASH and ASH occurred in a CH<sub>3</sub>COONa-HCl buffer system at pH 3 (optimum pH), where the concentration of H<sup>+</sup> ion during adsorption was not relatively changed.

**Table 3** Constant rate of Au(III) adsorption on adsorbents and linear coefficient in various kinetics models.

Kinetic model		ASH	Im-ASH
First order	$k (\min^{-1})$	0.18	$4 \times 10^{-3}$
	$R^2$	0.97	0.68
Second order	$k (\text{mM}^{-1} \text{min}^{-1})$	13.96	0.02
	$R^2$	0.87	0.76
Pseudo-first order	$k (\min^{-1})$	0.05	0.02
	$R^2$	0.99	0.71
Pseudo-second order	$k (\text{mM}^{-1} \text{min}^{-1})$	$2 \times 10^{-3}$	$1 \times 10^{-3}$
	$R^2$	1	1

#### Adsorption capacity

The adsorption capacity of Im-ASH and ASH toward Au(III) ion was studied by mixing the adsorbent with Au(III) ion solutions with various concentrations. The effect of Au(III) concentration on the adsorption is presented in Fig. 6. Langmuir isotherm model (eq. 8) [30] and Freundlich isotherm model (eq. 9) [31] were applied to evaluate the experimental data.

$$C_{\rm e}/q_{\rm e} = 1/KQ_{\rm max} + (1/Q_{\rm max})C_{\rm e}$$
 (8)

$$q_{\rm e} = k_{\rm f} C_{\rm e}^{\left(\frac{1}{n}\right)} \tag{9}$$

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where  $C_e$  is concentration of Au(III) in aqueous phase at equilibrium (µmol L<sup>-1</sup>),  $q_e$  is the amount of Au(III) on adsorbent at equilibrium (µmol g<sup>-1</sup>),  $Q_{max}$  is adsorption capacity (µmol g<sup>-1</sup>), K is Langmuir constant related to the measure of affinity of the absorbate for adsorbent (L mol<sup>-1</sup>),  $k_f$  is the Freundlich constant related to adsorption capacity of adsorbent (mg g<sup>-1</sup>), and n is the Freundlich exponent related to adsorption intensity. The experimental data show that the adsorption fits more with the Langmuir model than the Freundlich model. Langmuir and Freundlich parameter data are presented in Table 4. Im-ASH has lower capacity for Au(III) ion in comparison to ASH. In the surface of ASH, each ammonium group probably binds a Au(III) ion due to random distribution of the ammonium groups in the surface. On the contrary, in Im-ASH several ammonium groups are concentrated on a cavity assessible only for one Au(III) ion. The adsorption capacity data of Im-ASH and ASH compared to other adsorbents reported can be seen in Table 5, showing that adsorption capacity of Au(III) ion on Im-ASH and ASH is relatively higher than that on other adsorbents.



Fig. 6 Influence of Au(III) concentration on Au(III) adsorption onto ASH and Im-ASH (pH 3, contact time: 120 min, adsorbent dose:  $2.5 \text{ g L}^{-1}$ ).

Table 4 Langmuir parameters for Au(III) adsorption.

Adsorbent		Langmuir parameters					Freundlich parameters		
	$R^2$	$\frac{Q}{(\mathrm{mg}\;\mathrm{g}^{-1})}$	$p_{max} = (mmol g^{-1})$	$\frac{\Delta E}{(\text{kJ mol}^{-1})}$	$\frac{K \times 10^4}{(\text{L mol}^{-1})}$	$R^2$	$k_{\rm f}$ (mg g <sup>-1</sup> )	п	
ASH Im-ASH	0.93 0.98	131.97 76.14	0.67 0.39	21.17 23.61	0.49 1.29	0.92 0.96	24.47 9.92	1.01 0.97	

No.	Adsorbent	Capacity (mg/g)	Reference	
1	Nanometer TiO <sub>2</sub> immobilized on SG	3.56	[6]	
2	2-Mercaptobenzothiazol SG	4.50	[38]	
3	Chitosan	30.95	[39]	
4	N-Carboxymethyl chitosan	33.90	[39]	
5	Streptomyces aureoficiens	45.60	[40]	
6	RHA	28.22	[41]	
7	Activated carbon	35.88	[41]	
8	Chlorella vulgaris microorganism	10.34	[41]	
9	Modified thiol cotton fiber	68.00	[42]	
10	Nanometer-sized TiO <sub>2</sub>	22.63	[43]	
11	Epoxy-polyamine resin	120.00	[44]	
12	Cross-linked carboxymethyl chitin	11.86	[45]	
13	Cross-linked carboxymethyl chitosan	37.59	[45]	
14	Nanostructured Mn <sub>2</sub> O <sub>3</sub>	70.00	[46]	
15	3-(8-Quinolinylazo)-4-hydrobenzoic			
	acid nano-alumina	17.70	[47]	
16	L-Lysine cross-linked chitosan resin	70.34	[48]	
17	Multiwalled carbon nanotube	14.80	[49]	
18	N,N'-Bis-(2-hydroxybenzylidene)-			
	2,2'(aminophenylthio)ethane carbon nanotube	75.00	[50]	
19	ASH	131.97	this work	
20	Im-ASH	76.14	this work	

Table 5 Adsorption capacity of Au(III) on various reported adsorbents.

## Selectivity

Both Im-ASH and ASH adsorb Au(III) selectively in the Au(III)/Cu(II) system indicated by the k value greater than 1 (Table 6). At optimum pH (3.0), amine groups  $(-NH_2)$  in the surface of Im-ASH and ASH are protonated to form ammonium groups  $(-NH_3^+)$ . In that condition, Au(III) ions form complexes of  $[AuCl_4]^-$  anion; hence, "electrostatic pulls" between  $[AuCl_4]^-$  and  $-NH_3^+$  in the adsorbent occur. On the contrary, Cu(II) ions may not be adsorbed because "electrostatic pushes" occur between that metal ions and  $-NH_3^+$ . Because of "electrostatic pull" and "electrostatic push", Au(III) may be adsorbed selectively from Au(III)/Cu(II) solution on Im-ASH and ASH. However, the selectivity of Im-ASH to adsorb Au(III) is almost two times higher than that of ASH. Im-ASH may bind Au(III) more selectively due to specific cavities for Au(III) ions formed during the imprinting process.

ADSORBENT	$C_0 (\text{mmol/L})$		$K_d$ (L/g)		k	k'
	Au(III)	Cu(II)	Au(III)	Cu(II)		
ASH	0.5	0	6.97			
	0.5	0.5	4.02	0.04	100.50	
	0.5	1	5.38	0.03	179.33	
Im-ASH	0.5	0	1.86			
	0.5	0.5	3.73	0.02	186.50	1.86
	0.5	1	1.62	0.0044	368.18	2.12

**Table 6** Selectivity parameters of Au(III) and Cu(II) adsorption on ASH and Im-ASH.

## Effect of CI<sup>-</sup> ion

The effect of Cl<sup>-</sup> on Au(III) adsorption can be seen in Fig. 7. Im-ASH and ASH adsorb Au(III) almost completely in the solution without Cl<sup>-</sup>. The presence of Cl<sup>-</sup> in the solution decreases the ability of Im-ASH and ASH to adsorb Au(III). In the presence of 0.2 mol L<sup>-1</sup> Cl<sup>-</sup>, adsorbed Au(III) ions on both adsorbents decrease up to 50 %. Decreasing of the ability of Im-ASH and ASH to adsorb Au(III) is probably caused by the competition of Cl<sup>-</sup> ion and [AuCl<sub>4</sub>]<sup>-</sup> to bind ammonium group on the surface via an electrostatic interaction. The size of the Cl<sup>-</sup> ion is relatively smaller than that of [AuCl<sub>4</sub>]<sup>-</sup> complex; hence, the mobility of Cl<sup>-</sup> in the solution is relatively higher than [AuCl<sub>4</sub>]<sup>-</sup> complex, leading to the higher effectiveness of Cl<sup>-</sup> to interact with an ammonium group in the surface.



**Fig. 7** Influence of chloride ion concentration on Au(III) adsorption (Au(III) initial concentration: 50 mg L<sup>-1</sup>, pH 3, contact time: 120 min, adsorbent dose: 2.5 g L<sup>-1</sup>).

## CONCLUSIONS

Au(III) Im-ASH has been simply prepared by combining an ionic imprinting technique and sol-gel process using a precursor of  $Na_2SiO_3$  produced from the treatment of RHA. Adsorption of Au(III) is influenced by pH of the solution, the initial concentration of Au(III), the concentration of Cl<sup>-</sup>, and contact time. From the Langmuir isotherm model, the adsorption capacity of non-Im-ASH is higher than that of Au(III) Im-ASH. However, from the study on Au(III)/Cu(II) binary solution, it is found that in the presence of Cu(II), Im-ASH adsorbs Au(III) two times more selectively than ASH does. The kinetic studies indicate that adsorption of Au(III) ions on both Im-ASH and ASH fit the pseudo-second-order model.

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