Chitosan-functionalized natural magnetic particle@silica modified with (3-chloropropyl)trimethoxysilane as a highly stable magnetic adsorbent for gold(III) ion

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HIGHLIGHTS

- Functionalization of silica-coated magnetic particle (MP@SiO$_2$) with chitosan.
- Chitosan-functionalization enhanced adsorption capacity for Au(III) ion.
- (3-Chloropropyl)trimethoxysilane (CPTMS) strongly fixed chitosan on MP@SiO$_2$.
- Chitosan-functionalized MP@SiO2 linked with CPTMS was stable in an acidic solution.

GRAPHICAL ABSTRACT
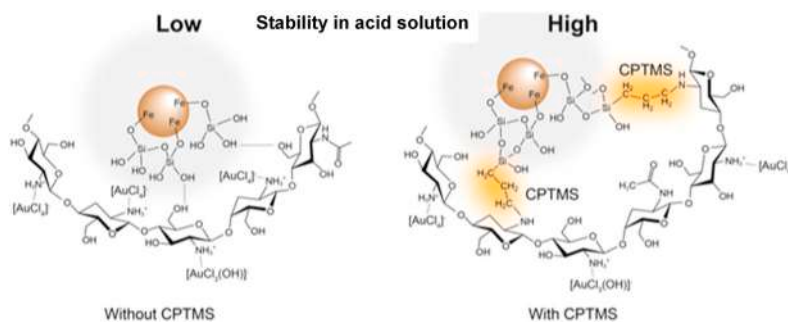
ARTICLE INFO

ABSTRACT

It is keenly desired to develop an environmentally benign and highly stable magnetic adsorbent for efficient recovery of Au(III) ion from an acidic solution. In the present study, we investigated the synthesis of magnetic adsorbents that the magnetic particles, which was prepared from natural iron sand, were modified with silica layer on which chitosan was fixed through 3-chloropropyltrymethoxysilane (CPTMS) by a sol-gel process. Since the magnetic particles were almost completely covered with the silica layer and chitosan was tightly fixed on it through CPTMS, the adsorbent was highly stable in an acidic solution with pH 3 or lower. Excess CPTMS significantly lowered the adsorption capacity for Au(III) ion, while lead to little improvement in the stability. Thus, 1 mmol of CPTMS against 4 mmol of chitosan gave the best magnetic adsorbent in terms of stability and adsorption capacity, of which the maximum was 112 mg g^{-1} for Au(III) ion at pH 5. The adsorbent showed high selectivity of Au(III) adsorption in the solution containing Cu(II) and Zn(II), and was reusable for two times

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keeping high selectivity without fatal decline in the adsorption performance. The magnetic adsorbent was separable from the solution simply with an external magnet, while the modification caused a slight decrease of the saturated magnetization.

1. Introduction

Gold is a precious metal with a variety of uses such as jewelry, electronic devices [1], medicines [2], and catalysts [3–5]. Gold is normally found in various minerals including chalcopyrite, pyrrhotite, pyrite, and arsenopyrite together with other metals. To produce pure gold from the minerals, processes need separation of ionic gold dissolved in the aqueous solution [6]. In addition, recently great efforts are devoted to recover gold from discarded home appliances and electronic devices like mobile phones and the separation in the aqueous gold solution is also a key step to achieve high recovery efficiency. An efficient separation process is, of course, helpful for the recovery of gold from waste solution produced from a gold plating processing. For the separation of gold in aqueous solution, adsorption technique has attracted much attention and been extensively studied because of many advantages, such as requiring less volume of toxic solvents and producing less amount of hazardous waste [7], being costless and easy handling, being effective even for low concentration gold [8], and adsorbents being reusable [9].

Silica is an inorganic material widely used as an adsorbent for various precious and rare metals including gold [10]. Silica has some advantages as an adsorbent, including large surface area, high thermal stability, high mechanical strength, and controllable particle and pore sizes [11]. The strong point of silica as an adsorbent is that the surface is readily modified with organic and inorganic functional groups [12] and indeed the modifications improve the adsorption performance. So far, the modifications of silica have been studied for adsorption of Au(III) ion in the solution [13–17]. In our previous study, it was demonstrated that the modification of silica with organosilane with amino group enhanced the adsorption capacity for Au(III) ion [18]. While single amino group works as an adsorption site for Au(III) ion, neighboring amino groups are more efficient for the adsorption due to cooperative complexation. In fact, Zhad et al. [19] reported that tris(2-aminoethyl)amine fixed on the surface through alkyl chain showed high adsorption performance for Au(III) ion in aqueous solution.

Poly-(D)glucosamine, namely chitosan, is a natural polysaccharide commercially produced from chitin by deacetylation [20]. Chitosan is rich in reactive amino groups that act as adsorption sites. In addition, it is reported that oxygens in glycosyl bonds in chitosan are involved in the complexation to Au(III) ion [21]. Thus, chitosan would be a useful modifier for silica to produce the high-performance adsorbent. For instance, Han et al. reported that coating of Na-X zeolite with chitosan significantly improved the adsorption performance for arsenate ion in an aqueous solution [22]. However, chitosan has fatal drawbacks as a modifier; it is highly soluble in an acidic solution and weak mechanical strength by nature [23], leading to poor stability of the silica-chitosan hybrid adsorbents in acidic solution, which is common conditions for the separation of Au(III) ion in aqueous solution.

Thus, addition of the coupling agents such as glutaraldehyde, epoxy, and chlorine compounds have been investigated to improve the stability of chitosan on the surface [24]. Fujiwara et al. [25] synthesized a cross-linked chitosan resin modified with L-lysine for adsorption of Au(III) ion and demonstrated L-lysine suppressed the detachment of chitosan from the material. 3-Chloropropyltrimethoxysilane (CPTMS) is a common coupling agent widely used for the modification of organic-inorganic hybrid materials [26]. Since chlorine in CPTMS strongly interacts or forms a covalent bond with amino group in chitosan and meanwhile methoxysilyl groups react with hydroxy groups on solid materials, CPTMS acts as a glue to improve the stability of chitosan in hybrid materials especially in acidic solution [27].

The adsorption performances of the modified siliceous adsorbents for Au(III) ion are often evaluated via a batch technique for its simplicity. However, it often happens that separation of the adsorbent become problems especially for large scales operation, because conventional separation methods such as filtration, centrifugation, and decantation [28] are impractical and ineffective in the large-scare process. In order to overcome the problem, magnetic adsorbents readily separable by external magnetic field has been developed by compositing the adsorbent with magnetic materials like magnetite (Fe_3O_4) [29]. Chang and Chen [30] reported chitosan-coated Fe_3O_4 nano-adsorbent being useable for the adsorption of Au(III) ion. Donia et al. [31] proposed a method for the modification of Fe_3O_4 with chitosan through a reaction between chitosan and polymeric Schiff base. Indeed, both magnetic adsorbents showed the improved adsorption capacities for Au(III) ion in aqueous solution, but their stabilities were unknown despite the fact that both Fe_3O_4 and chitosan are soluble in acidic solutions.

While synthetic magnetite is often utilized as a magnetic core for siliceous magnetic adsorbents [29], recently natural magnetic materials such as iron sand have gained much attention in view of environmental friendliness [32]. Main component of natural iron sand is iron oxides including magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3) [33]. Iron sand provides several advantages such as ease of obtaining and low cost due to its availability and thus is a promising material especially for environmentally benign mining and resource recovery as well as chemical processes.

In the present study, we investigated functionalization of natural magnetic particles with silica, chitosan, and CPTMS by a concurrent sol-gel process. The reason for applying the sol-gel process is to minimize the damage to the magnetic core during the modification owing to mild reaction temperature and to effectively introduce chitosan onto silica layer over the magnetic particle because of the concurrent progression of the formation of the silica layer and the modification with chitosan. We investigated in detail the role of CPTMS in the adsorbents for the stability in acidic solutions and adsorption properties for Au(III) ion.

2. Experimental

2.1. Materials

The natural magnetic particles (denoted as MP) were prepared from iron sand collected in Bugel Beach, Yogyakarta. Magnetic substance was separated from the iron sand with a permanent magnet [34] and was grounded in a mortar with a pestle. The obtained powder was sieved using a sieve with 200 mesh in screen size and was washed with distilled water, followed by dried at 95 °C for 18 h. Then, the material was treated in 10% hydrofluoric acid at 80 °C for 2 h, followed by washed with excess distilled water until pH of the solution was neutral. Finally, the solid was dried at 95 °C for 18 h to obtain MP.

Chitosan with deacetylated degree of 80% or more was purchased from Ocean Fresh (Bandung, Indonesia). The other chemicals used in this study, including hydrochloric acid (37%), acetic acid (>99%), aqueous ammonia (27%), sodium hydroxide (100%), standard solutions of Au(III), Cu(II) and Zn(II), liquid glass (25.5–28.5% SiO_2 and 7.5–8.5% Na_2O), and CPTMS were purchased from Merck (Germany), and used as received without any further pretreatment.

2.2. Synthesis of magnetic adsorbents covered with chitosan-modified silica through a concurrent sol-gel process

The functionalization of MP through a concurrent sol-gel process was

Table 1
Magnetic adsorbents synthesized in this study.

Magnetic adsorbent	Amount added/mmol	
	CPTMS[a]	chitosan
MP@[Chi-SiO$_2$]	0	4
MP@[Chi-CPTMS(1/4)-SiO$_2$]	1	4
MP@[Chi-CPTMS(2/4)-SiO$_2$]	2	4
MP@[Chi-CPTMS(3/4)-SiO$_2$]	3	4
MP@[Chi-CPTMS(4/4)-SiO$_2$]	4	4
MP@SiO$_2$	0	0

[a] 3-chloropropyltrimethoxysilane.
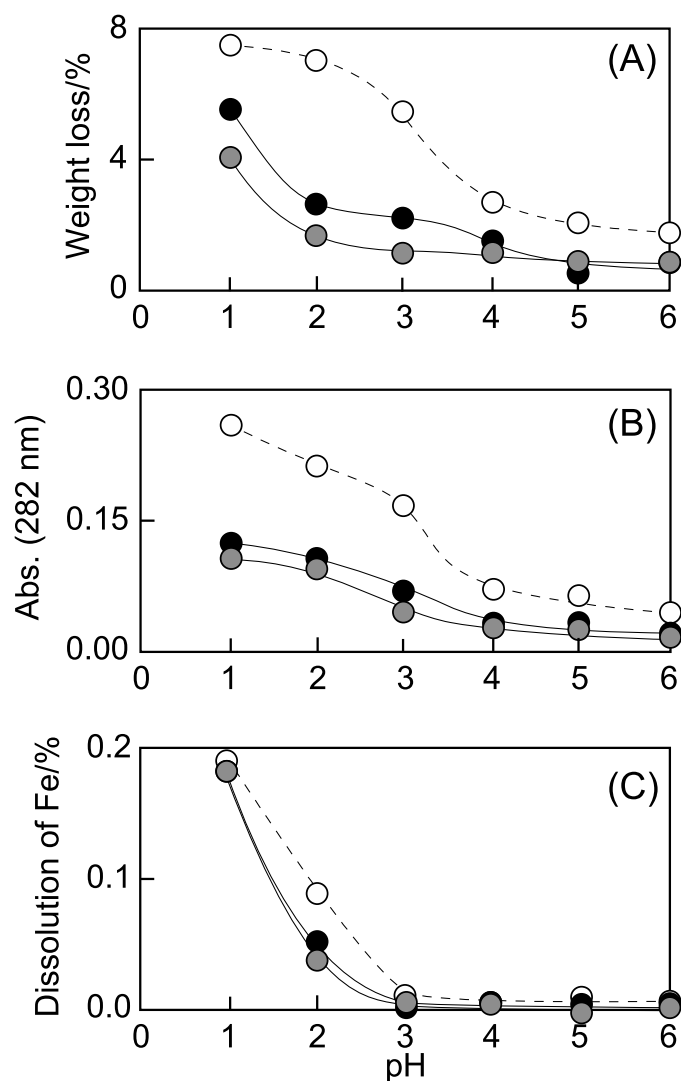
Fig. 1. Stability of the magnetic adsorbents in acidic solution with different pH. (A) weight loss, (B) dissolution of chitosan, and (C) dissolution of Fe. (○) MP@[Chi-SiO$_2$], (●) MP@[Chi-CPTMS(1/4)-SiO$_2$], and (●) MP@[Chi-CPTMS(3/4)-SiO$_2$]. Dissolution of chitosan and dissolution of Fe were estimated by UV–vis spectroscopy and atomic absorption spectrometry, respectively.

performed as follows. MP (0.5 g) was dispersed in a solution prepared by diluting 1.0 mL (6.0 mmol) of liquid glass with 1 mL of distilled water. The pH of the resulting suspension was adjusted to 10 by the addition of hydrochloric acid dropwise. The suspension was then poured into an aqueous solution prepared by mixing 0.18 mL (1.0 mmol) of CPTMS and 33 mL (4.0 mmol) of 2 wt% chitosan solution with 1% acetic acid. Aqueous ammonia was added into the mixture until pH 7 and then the obtained gel was allowed to stand at room temperature for 24 h. The

solid was separated by applying external magnetic field, and then dried at 60 °C for 24 h. The obtained adsorbent is denoted as MP@[Chi-CPTMS(1/4)-SiO$_2$], in which the figure in parenthesis is the molar amount of CPTMS and chitosan in mmol, respectively. The adsorbents with CPTMS/chitosan = 2/4, 3/4, and 4/4 were prepared with the similar manner to that for MP@[Chi-CPTMS(1/4)-SiO$_2$], but the amounts of CPTMS were increased keeping that of chitosan constant (Table 1). The syntheses were also conducted without CPTMS, and without CPTMS nor chitosan and the obtained adsorbents are denoted as MP@[Chi-SiO$_2$] and MP@SiO$_2$, respectively.

2.3. Stability test in acidic solution

The magnetic adsorbent (20 mg) was added to an aqueous solution (10 mL) with different pH (= 1, 2, 3, 4, 5, and 6), which was adjusted by the addition of hydrochloric acid (0.1 M) or aqueous solution of NaOH (0.1 M). The suspension was shaken at room temperature for 2 h. Then, the solid was separated with a magnet, dried at 110 °C for 4 h and weighted to estimate the weight loss in the solution. The concentration of Fe(III) dissolved in the solution was measured by atomic absorption spectrometry (AAS, AnalytikJena, ContrAA® 300, Germany), and the dissolution of chitosan was checked using a UV–Vis spectrophotometer (Shimadzu, UV-1700, Japan).

2.4. Adsorption experiment

Adsorption properties of the magnetic adsorbents for Au(III) ion were evaluated in a batch process. The aqueous solutions containing Au (III) ion with different concentrations (25–400 mg L^{-1}) were prepared by diluting Au(III) standard solution (1000 mg L^{-1}) with pure water. The pH of the solution was varied from 1 to 6 by the addition of hydrochloric acid or an aqueous solution of NaOH.

The magnetic adsorbent (20 mg) was added to 10 mL of the aqueous Au(III) solution and then the suspension was shaken at a speed of 200 rpm and room temperature for 2 h. The solid was separated by a magnet and the concentration of Au(III) ion in the solution was analyzed by AAS. Two well-known adsorption models, namely Langmuir [35] and Freundlich [36], were applied to analyze the adsorption isotherms for Au(III) ion over the magnetic adsorbents.

2.5. Influence of other metal ions on adsorption performance and reusability test of the magnetic adsorbent

The influence of other metal ions on the adsorption of Au(III) over MP@[Chi-CPTMS(1/4)-SiO$_2$] was investigated in a solution containing Cu(II) and Zn(II) in addition to Au(III). The concentrations of Au(III), Cu (II) and Zn(II) were 14.5, 1600, and 18100 mg/L, respectively, which are similar to those found in a typical gold mining rock solution. The adsorption experiment was performed with a similar manner to that described in 2.4 (Adsorption experiment) except for using the solution containing Au(III), Cu(II) and Zn(II).

After the adsorption, desorption of the metal ions and repeated use of the adsorbent were investigated as follows. The spent adsorbent, which was separated from the solution by an external magnet, was added to 10 mL of 6%-thiourea solution in 0.1 M HCl, and the suspension was shaken at a rate of 200 rpm and room temperature for 1 h to promote the desorption. Then the adsorbent was separated by an external magnet and the resulting solution was analyzed by AAS to determine the concentrations of the metal ions desorbed from the adsorbent. The collected adsorbent was afforded to second use (reuse) and for characterization with FTIR, XRD, and SEM after drying at 60 °C for 2 h. Reusability test was performed for five repetitions in total.

2.6. Characterization of magnetic adsorbents

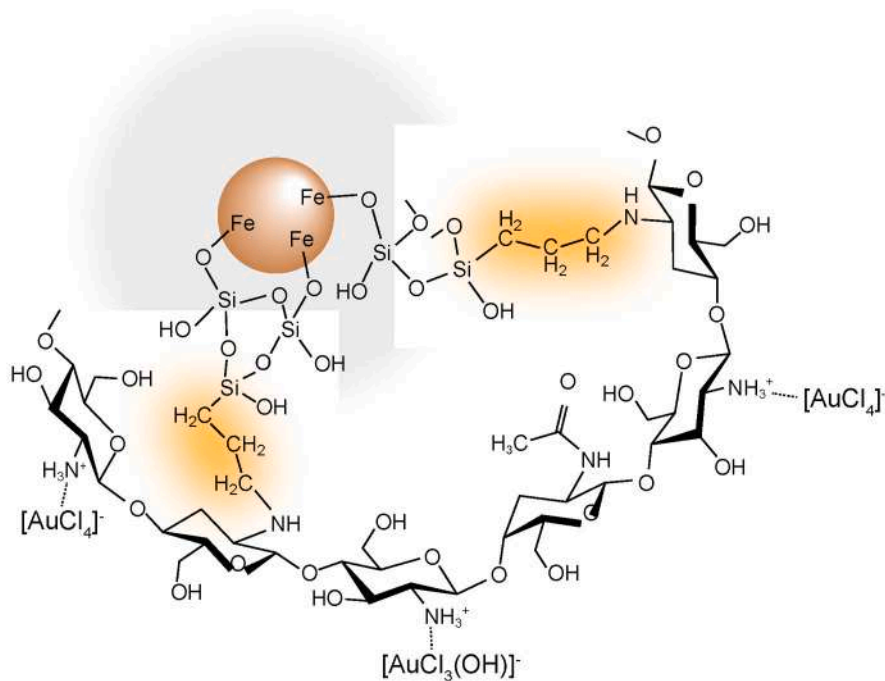The magnetic adsorbents was characterized by multiple techniques
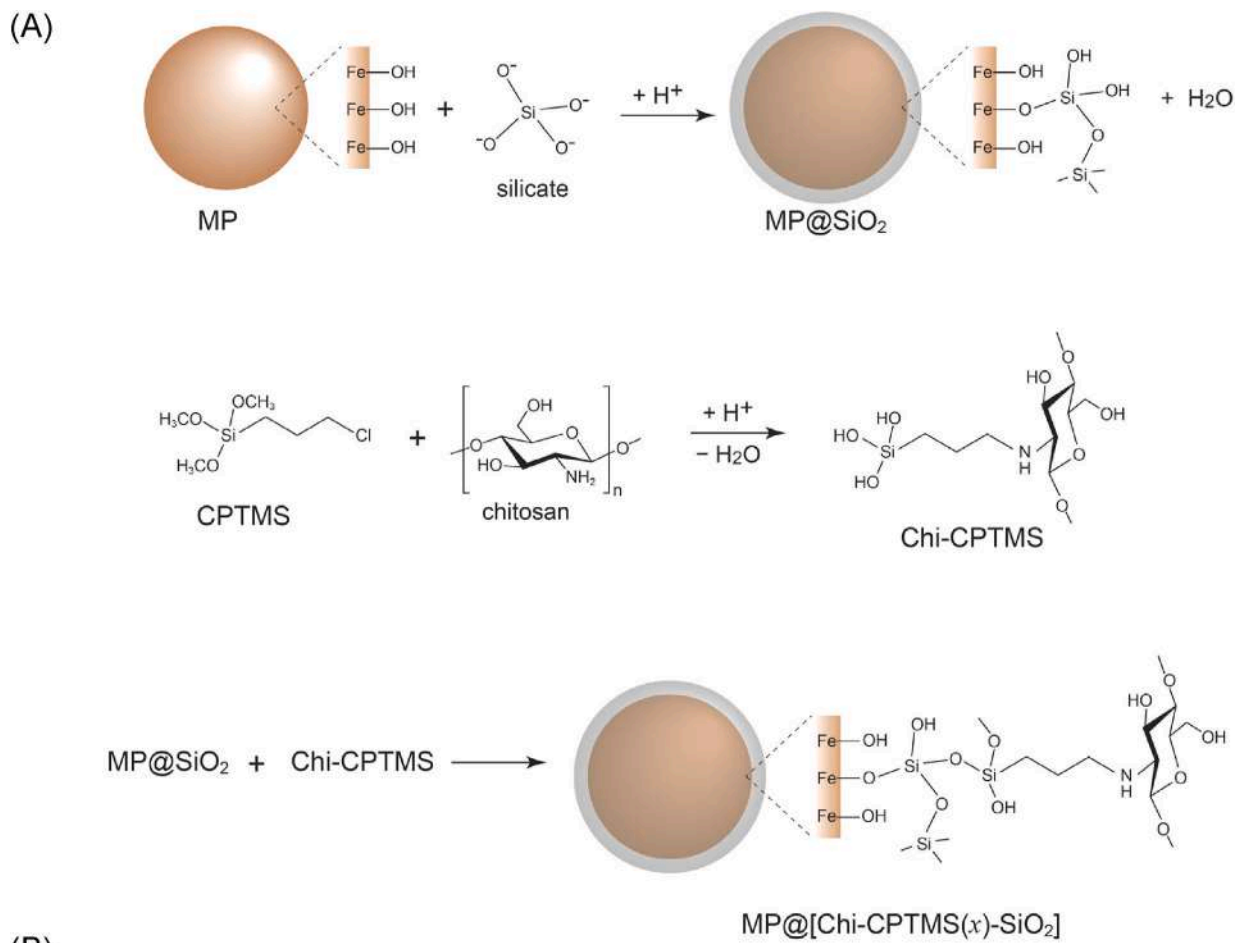
Fig. 2. Schematic illustrations of (A) process for the formation of the silica layer coupled with chitosan through CPTMS and (B) structure of MP@[Chi-CPTMS (x)-SiO$_2$].
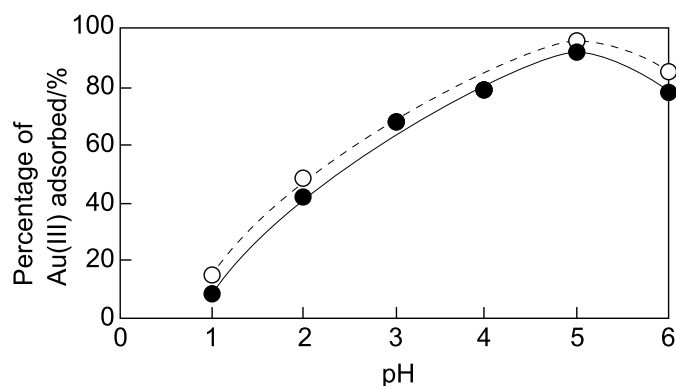
Fig. 3. Adsorption of Au(III) ion over (○) MP@[Chi-SiO$_2$] and (●) MP@[Chi-CPTMS(1/4)-SiO$_2$]. Conditions: magnetic adsorbent, 20 mg; volume of solution, 10 mL; concentration of Au(III) ion, 25 mg/L; temperature, room temperature; and time, 2 h. Concentration of Au(III) ion in the solution was determined by atomic adsorption spectrometry.

using a Fourier-transform infrared spectrometer (Shimadzu, IRPrestige-21, Japan), X-ray diffractometer (Rigaku, Multiflex, Japan), scanning electron microscope (JEOL, JED-2300 type, Japan), vibrating sample magnetometer (Oxford, VSMI.2H, UK), thermogravimetric analyzer (NETZSCH STA 449F1, Germany), and the ultraviolet–visible spectrometer.

In addition, isoelectric point (pH$_{PZC}$) of the magnetic adsorbent was determined by a conventional pH drift method. The magnetic adsorbent (10 mg) was added to 10 mL of aqueous NaCl solution (0.01 M) with different pH. The suspension was shaken at room temperature for 2 h, and then allowed to stand for 48 h. After that, the solid was separated by an external magnet and pH of the residual solution was measured. In this method, the pH that final pH was identical to initial one on the plot of initial pH versus final one corresponds to pH$_{PZC}$.

3. Results and discussion

3.1. Stability of the magnetic adsorbents in acidic solution

As mentioned in the introductory part, the magnetic adsorbents should be stable in acidic solution for adsorption separation of Au(III) ion. Thus, first of all, the stability of the adsorbents was examined in acidic solutions with pH 1–6 and were evaluated with respect to the weight loss, dissolution of chitosan and dissolved amount of Fe. The dissolution of chitosan was confirmed with the absorbance of the solution at 282 nm.

Fig. 1 shows the results of the stability test for MP@[Chi-SiO$_2$], MP@[Chi-CPTMS(1/4)-SiO$_2$], and MP@[Chi-CPTMS(3/4)-SiO$_2$], which were chosen as typical magnetic adsorbents for comparison. The weight loss, dissolution of chitosan, and dissolved amount of Fe were increased with decrease of pH of the solution for all the adsorbents. Since amino groups in chitosan are protonated in acidic solution, the solubility of chitosan is increased, causing the elimination of chitosan from the magnetic adsorbents. As Fig. 1 clearly shows, the magnetic adsorbents with CPTMS, namely MP@[Chi-CPTMS(1/4)-SiO$_2$] and MP@[Chi-CPTMS(3/4)-SiO$_2$], were much more stable than that without CPTMS (MP@[Chi-SiO$_2$]), indicating that CPTMS improved the stability of the adsorbents in acidic solution. As a result, the adsorbent with CPTMS showed high stability in the solution with pH 3 or higher. Since chlorine at the one end of CPTMS strongly interacts with or forms a covalent bond with amino group in chitosan and methoxysilyl groups at the other end react with silanol groups on silica [27], it is considered that CPTMS acts as a linker between chitosan and the silica layer on the magnetic adsorbent (Fig. 2).

MP@[Chi-CPTMS(3/4)-SiO$_2$] was more stable than MP@[Chi-CPTMS(1/4)-SiO$_2$], but the improvement in the stability was only little. In other words, 1 mmol of CPTMP for 4 mmol of chitosan was enough to tightly hold chitosan on the adsorbent. Thus, it is considered that MP@[Chi-CPTMS(1/4)-SiO$_2$] was better than MP@[Chi-CPTMS(3/4)-SiO$_2$] to make a good balance between stability and adsorption capacity. This is discussed again later in Section 3.2.

3.2. Adsorption of Au(III) on magnetic adsorbents and influences of chitosan and CPTMS on adsorption performance

Because pH of the solution has often a major impact on the adsorption capacity, the influence of pH on the adsorption of Au(III) ion on the magnetic adsorbents was investigated in the solutions with pH 1–6. To know the effect of CPTMS on the adsorption properties, the adsorption capacity of MP@[Chi-CPTMS(1/4)-SiO$_2$] was compared with that of MP@[Chi-SiO$_2$]. Fig. 3 shows the influence of pH on the adsorption amounts over MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)-SiO$_2$], where the adsorption amounts were expressed as percentage of Au(III) ion removed from the solution, namely recovery rate. The experiments were performed using the solution containing 25 mg L^{-1} of Au(III) ion.

Regardless of the presence or absence of CPTMS, both adsorbents showed a similar trend against pH of the solution and had the maximum at pH 5. It indicates that similar active sites namely amino groups in both adsorbents are responsible for the adsorption. The appearance of the maximum at pH 5 is explainable in terms of pH$_{PZC}$ of the adsorbents, which is discussed later.

Fig. 4 shows the results for determination of pH$_{PZC}$ for MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)-SiO$_2$]. Based on the data shown in Fig. 4, pH$_{PZC}$ for both adsorbents were ca. 7.5, meaning that the surface is positively charged in acidic solutions, leading to the protonation of amino groups in chitosan to form –NH$_3^+$, as reported [37]. In such acidic solution with Cl$^-$, Au(III) ion is present as Cl$^-$-containing anionic species like [AuCl$_4$]$^-$ and [AuCl$_{4-x}$(OH)$_x$]$^-$ [38] and it is plausible that Au(III) ion strongly interact with chitosan through electrostatic interaction [39], which is responsible for the large adsorption amount of Au(III) ion on the adsorbents.

In the solution with pH lower than 5, the adsorption amounts were rather small. For the adsorption experiments at low pH conditions, the concentration of Cl$^-$ became high, because the solutions acidified with hydrochloric acid were used. Thus, it is plausible that high concentration Cl$^-$ in the solution inhibited the adsorption of Au(III) ion on the protonated amino and acetoamide groups of chitosan on the magnetic adsorbents. In the solution with pH higher than 5, on the other hand, the adsorption amount was also decreased. This is probably because change in the gold ion species. It is known that [AuCl(OH)$_2$]$^-$ and [AuCl(OH)$_3$]$^-$ are predominant in the reaction solution with pH more than 6 [38]. Thus, substitution of Cl$^-$ with OH$^-$ on [AuCl$_{4-x}$(OH)$_x$]$^-$ increases the preference of the complex to stay in the solution owing to making strong hydrogen bond with water molecules, leading to small adsorption amount.

Effect of the modification with chitosan as well as the silica layer on the adsorption capacity for Au(III) ion was investigated by comparison of the adsorption capacities between MP, MP@SiO$_2$, and MP@[Chi-SiO$_2$] in the solution at pH 5. Fig. 5 shows the adsorption amounts of Au(III) ion over the magnetic adsorbents. The adsorption experiments were performed under the similar conditions to those shown in Fig. 3. As Fig. 5 clearly demonstrates, the functionalization of the magnetic adsorbent with chitosan significantly increased the adsorption capacity, while the silica layer had only little impact, indicating that amino groups in chitosan are major adsorption sites for Au(III) ion. The adsorption site is further discussed later in relation to the decrease of the adsorption capacity caused by CPTMS-modification.

To investigate the influence of CPTMS on the adsorption capacity for Au(III) ion, adsorption isotherms of MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(x)-SiO$_2$] (x = 1/4, 2/4, 3/4, and 4/4) were measured. The initial concentrations of Au(III) ion were changed from 25 to 400 mg L^{-1}, while

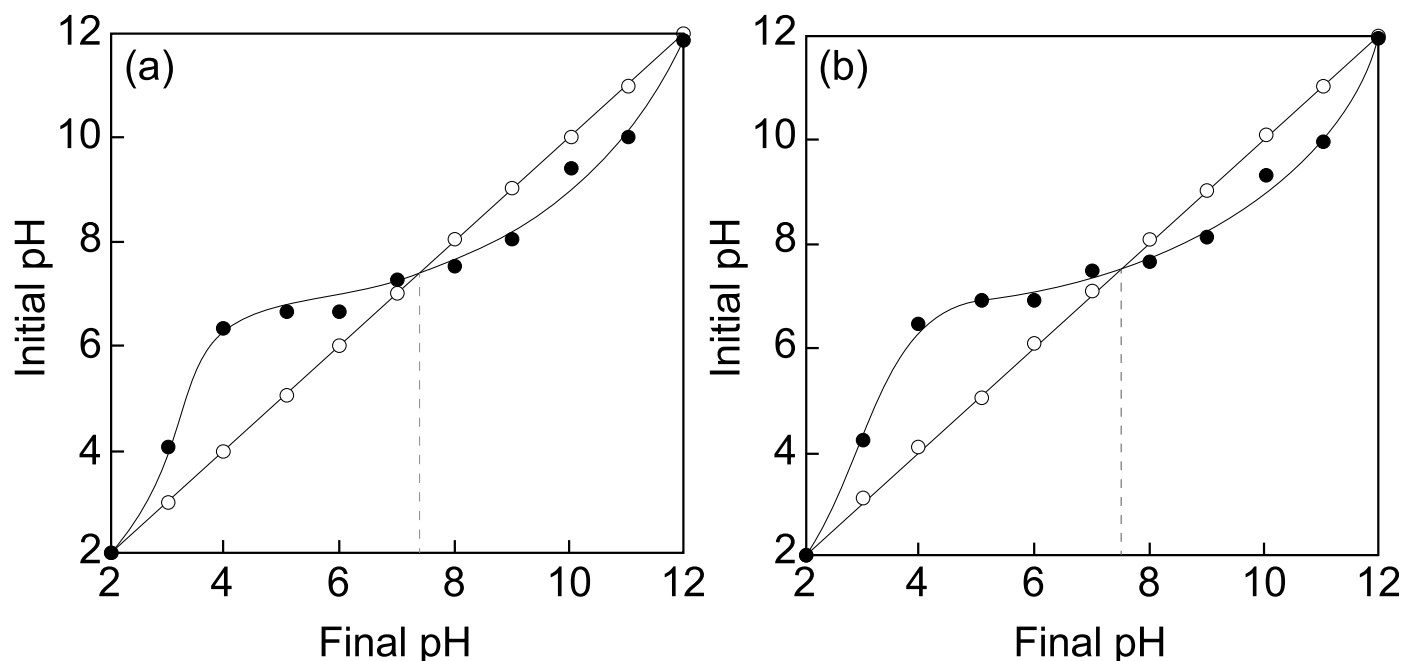**Fig. 4.** Determination of isoelectric point (pH_{PZC}) for (a) MP@[Chi-SiO$_2$] and (b) MP@[Chi-CPTMS(1/4)-SiO$_2$]. (○) in the absence of magnetic adsorbent and (●) in the presence of magnetic adsorbent. Conditions: magnetic adsorbent, 10 mg; solution, aqueous NaCl solution (0.01 M); volume of solution, 10 mL; and temperature, room temperature. pH of the solution was adjusted adding 0.1 M HCl or 0.1 M NaOH solution. The suspension was shaken at room temperature for 2 h, and then allowed to stand for 48 h. After that, the solid was separated by an external magnet and pH of the residual solution was measured.

pH was fixed to 5. The adsorbed amounts of Au(III) at equilibrium concentration (q_e) are plotted as a function of the equilibrium concentrations (C_e) in Fig. 6. The adsorption amount increased sharply at low concentration and then approached a constant. These adsorption isotherms were analyzed by applying Langmuir's and Freundlich's isotherm models to obtain the adsorption parameters, which are summarized in Table 2. Based on the R^2 values, it can be concluded that the adsorption isotherms follow the Langmuir isotherm model, indicating that the adsorption sites are uniform and multilayer adsorption of Au (III) ion does not occur over the magnetic adsorbents.

It is noted that the maximum adsorption capacities (q_{max}) were decreased with increase in the amounts of CPTMS added to the magnetic adsorbents, while the equilibrium constants (K_L) were almost the same each other, indicating that CPTMS did not change the property of the adsorption sites, but decreased only the number of them. In fact, q_{max} was linearly decreased with increase in the amount of CPTMS (Fig. 7). Since most of the adsorption sites on the magnetic adsorbents were present in chitosan as demonstrated in Fig. 5, it is reasonable that chlorine in CPTMS strongly interacts with (-CH$_2$Cl –HNH-) or forms a covalent bond (–CH$_2$–NH-) with the amino groups, consequently decreasing the maximum adsorption capacities. While the presence of CPTMS is essential for stabilization of the magnetic adsorbent, the excess CPTMS is disadvantageous as mentioned before. As discussed in the previous section, the addition of excess CPTMS did not significantly change the stability of the magnetic adsorbents. Therefore, we concluded that MP@[Chi-CPTMS(1/4)-SiO$_2$] was the best of magnetic adsorbents studied in terms of stability in acidic solutions as well as adsorption capacity.

3.3. Selectivity of Au(III) adsorption and reusability of MP@[Chi-CPTMS (1/4)-SiO$_2$]

Selectivity of Au(III) adsorption over other metal ions and reusability test for MP@[Chi-CPTMS(1/4)-SiO$_2$] were performed in the solution containing Au(III), Cu(II) and Zn(II). Fig. 8 is the result of the five repetitive use of MP@[Chi-CPTMS(1/4)-SiO$_2$] for the adsorption test.

Recovery rate of each ion was defined as eq. (1),

$$Recovery\ rate\ (\%) = \frac{[M]_0 - [M]_{2h}}{[M]_0} \times 100 \tag{1}$$

where $[M]_0$ and $[M]_{2h}$ are initial concentration of metal ion and concentration after 2 h adsorption, respectively. While recovery rate of Au (III) for the first use was 80.9%, was slightly decreased for the second
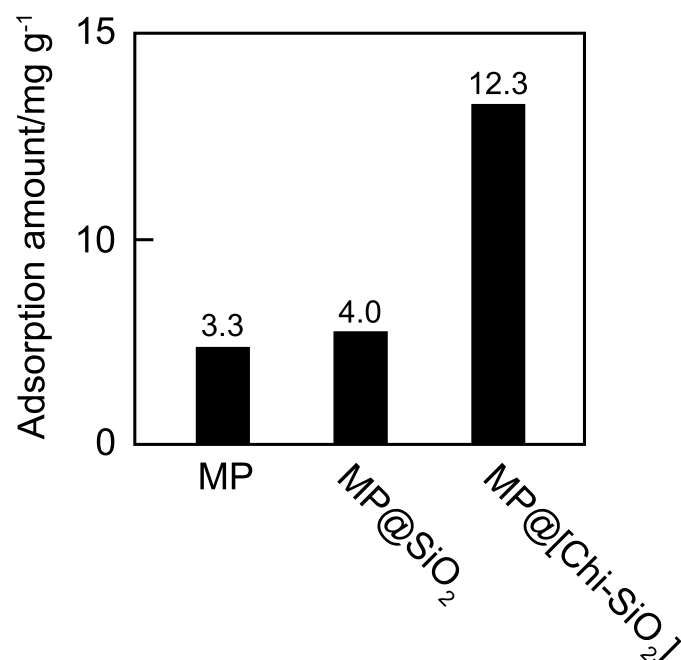

Fig. 5. Adsorption amount of Au(III) ion over MP, MP@SiO$_2$, and MP@[Chi-SiO$_2$]. Conditions: magnetic adsorbent, 20 mg; volume of solution, 10 mL; concentration of Au(III) ion, 25 mg/L; pH of the solution, 5.0; temperature, room temperature; and time, 2 h.
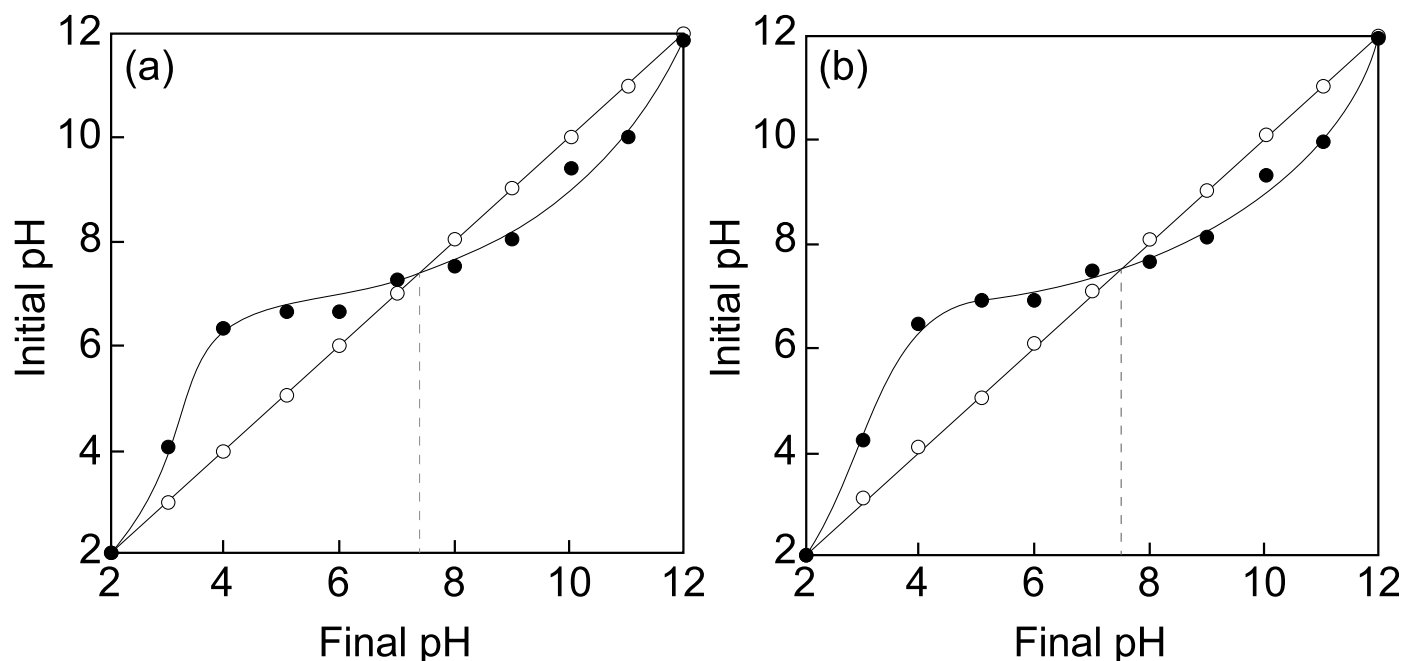
Fig. 6. Adsorption isotherms of Au(III) ion for MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(*x*)-SiO$_2$]. Conditions: magnetic adsorbent, 20 mg; volume of solution, 10 mL; pH of the solution, 5.0; temperature, room temperature; and time, 2 h.

and third uses, but was down to 39.2% for the fifth one. The decrease in the adsorption capacity with the repeated use was probably due to the damage of chitosan in the acidic solution which lead to the reduction of the number of protonated amino groups and/or presence of residual other metal ions which blocked the active sites from the adsorption of Au(III) ion.

It should be noted that the recovery rates of Cu(II) and Zn(II), which were 0.22 and 0.07%, respectively, were significantly lower than that of Au(III), for the first use, meaning high selectivity of Au(III) adsorption on MP@[Chi-CPTMS(1/4)-SiO$_2$]. In fact, selectivities of Au(III) adsorption against that of Cu(II) and Zn(II) defined as eq. (2) were very high (Table 3).

$$Selectivity\,of\,Au(III)\,adsorption\,(\alpha_{Au/Cu\,or\,Zn}) = \frac{Recovery\,rate\,of\,Au(III)}{Recovery\,rate\,of\,Cu(II)\,or\,Zn(II)}$$
(2)

While the recovery rates of Cu(II) and Zn(II) were increased with reuses, those were very low, being 0.53 and 0.14%, respectively, even for the fifth use. Thus, MP@[Chi-CPTMS(1/4)-SiO$_2$] had still high

selectivity of Au(III) adsorption. The high selectivity of Au(III) adsorption on MP@[Chi-CPTMS(1/4)-SiO$_2$] can be explained based on the species present in the solution. As mentioned before, Au(III) was present as [AuCl$_4$]$^-$ and [AuCl$_3$OH]$^-$ in the solution at pH 5. In contrast, Cu(II) and Zn(II) were present as hydrated cations in the solution. Therefore, Au(III) was selectively interacted with protoned amino groups on the adsorbent.

3.4. Characterization of MP@[Chi-CPTMS(1/4)-SiO$_2$]

The XRD patterns of MP, MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$] are shown in Fig. 9. MP gave a diffraction pattern assignable to magnetite Fe$_3$O$_4$ and the crystallite size estimated by applying Scherrer's equation to (311) diffraction line was 25 nm. For MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$], a halo peak at 2θ of 20–27° due to amorphous silica was observed in addition to the clear diffraction

Table 2
Parameters obtained by applying Langmuir and Freundlich equations for the adsorption isotherms of Au(III) ion.

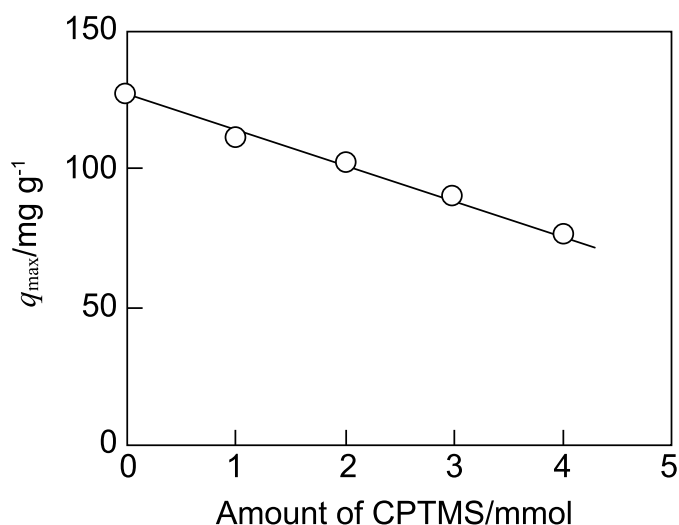| Magnetic adsorbent	Langmuir model			Freundlich morel		
	R^2	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1})	n
MP@[Chi-SiO$_2$]	0.9982	127	0.18	0.9108	24.6	2.86
MP@[Chi-CPTMS(1/4)-SiO$_2$]	0.9996	112	0.15	0.8346	19.8	2.68
MP@[Chi-CPTMS(2/4)-SiO$_2$]	0.9995	103	0.27	0.9377	25.9	3.34
MP@[Chi-CPTMS(3/4)-SiO$_2$]	0.9984	90	0.25	0.9292	27.1	3.91
MP@[Chi-CPTMS(4/4)-SiO$_2$]	0.9981	76	0.18	0.8825	20.0	3.58

Fig. 7. Relationship between the maximum adsorption capacity (q_{max}) and amount of CPTMS added to the magnetic adsorbents.
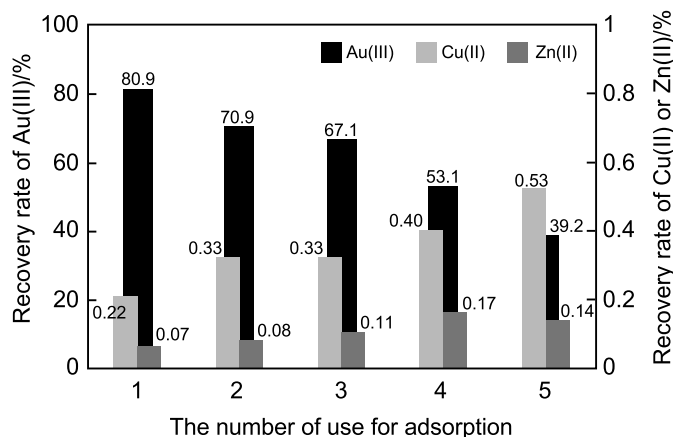
Fig. 8. Recovery rates of Au(III), Cu(II) and Zn(II) and repeated use of MP@[Chi-CPTMS(1/4)-SiO$_2$] for the adsorption experiments.

Table 3
Selectivity of Au(III) adsorption against Cu(II) and Zn(II) on MP@[Chi-CPTMS(1/4)-SiO$_2$] for five repetition of adsorption-desorption in the solution containing Cu(II) and Zn(II) in addition to Au(III).[a]

Repetation	$\alpha_{Au/Cu}$[b]	$\alpha_{Au/Zn}$[b]
1	368	1156
2	215	886
3	203	610
4	133	312
5	74	280

[a] Adsorption experiments were performed in the solution containing 14.5 mg/L Au(III), 1600 mg/L Cu(II) and 18100 mg/L Zn(II) at room temperature for 2 h. After the adsorption, the adsorbent was treated in 6% thiourea solution in 0.1 M HCl and the was afforded to the next adsorption experiment.
[b] Selectivity of Au(III) adsorption is defined as recovery rate of Au(III) divided by that of Cu(II) or Zn(II).
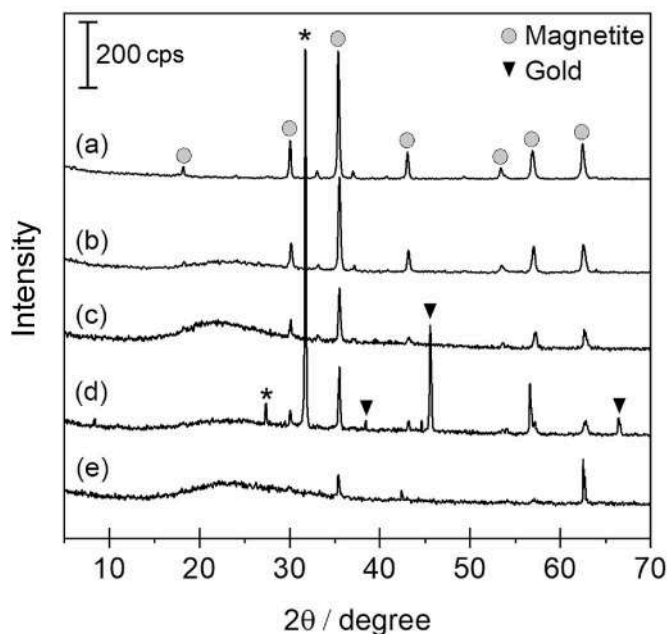

Fig. 9. XRD patterns of (a) MP, (b) MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)-SiO$_2$] (c) before adsorption, (d) after adsorption and (e) after desorption of Au(III).
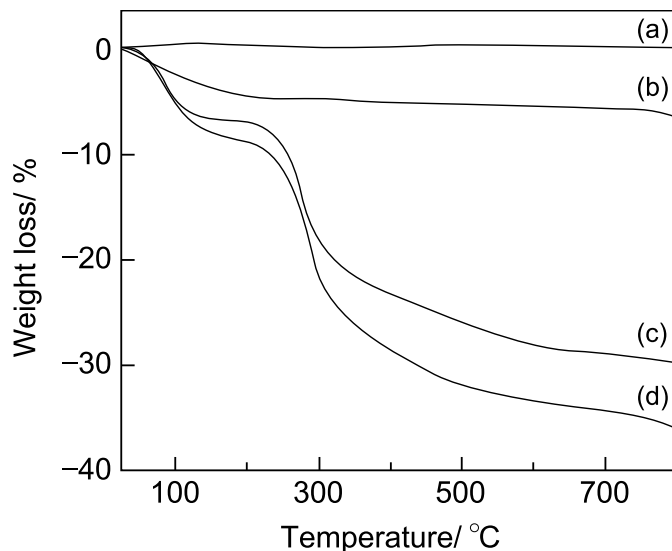

Fig. 10. TG profiles for (a) MP, (b) MP@SiO$_2$, (c) MP@[Chi-SiO$_2$] and (d) MP@[Chi-CPTMS(1/4)-SiO$_2$] taken in O$_2$.
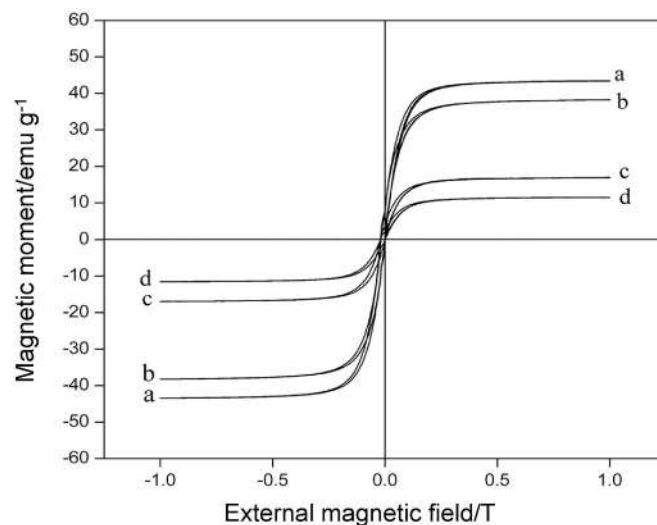

Fig. 11. Magnetic moments for (a) MP, (b) MP@SiO$_2$, (c) MP@[Chi-SiO$_2$] and (d) MP@[Chi-CPTMS(1/4)-SiO$_2$].

pattern of Fe$_3$O$_4$. A similar result is reported by Lei et al. [39]. It is noted that the crystallite size of the MP core (Fe$_3$O$_4$) did not change by the modifications with the silica layer, chitosan, and CPTMS.

Fig. 10 shows TG profiles taken in O$_2$ for MP, MP@SiO$_2$, MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$]. There was little weight loss for MP. MP@SiO$_2$ showed ~6% weight loss due to desorption of physically adsorbed water and condensation of silanol groups of SiO$_2$ [40]. In contrast to them, MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$] exhibited larger weight losses, which were 23.0 and 28.8 wt%, respectively, in the temperature between 250 and 800°C, due to combustion of organic moieties [41]. The larger weight loss for MP@[Chi-CPTMS(1/4)SiO$_2$] than that for MP@[Chi-SiO$_2$] was attributed to the presence of CPTMS in the former.

Influence of the modifications with chitosan and CPTMS as well as the silica layer on the magnetic properties was investigated with the magnetic moment taken on a vibrating sample magnetometer (Fig. 11). The magnetic moments of all the magnetic adsorbents including MP,
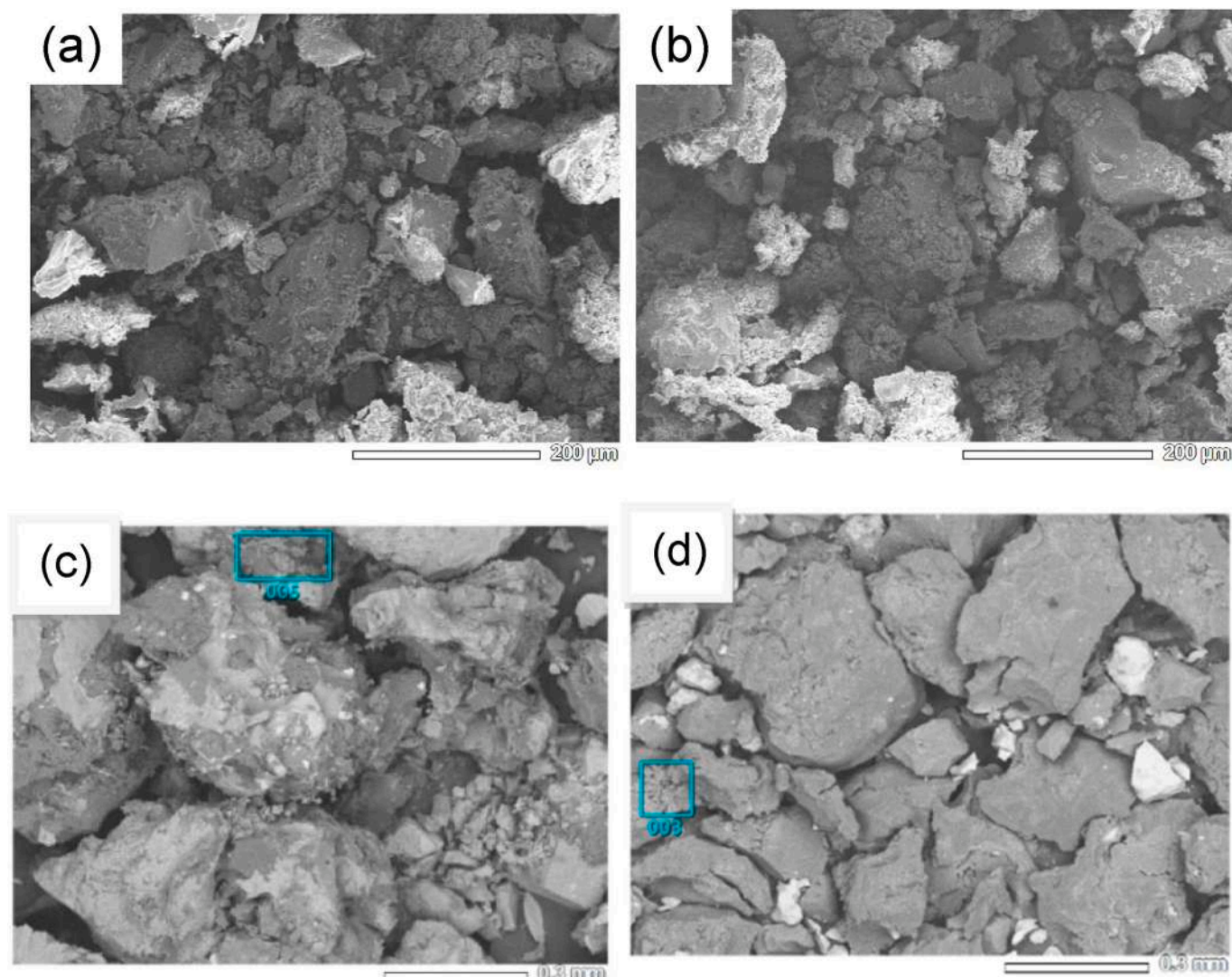
Fig. 12. SEM images of (a) MP@[Chi-SiO$_2$], (b) MP@[Chi-CPTMS(1/4)-SiO$_2$], (c) MP@[Chi-CPTMS(1/4)-SiO$_2$] after adsorption, and (d) MP@[Chi-CPTMS(1/4)-SiO$_2$] after desorption.

Table 4
Surface compositions of magnetic adsorbents estimated by EDX analysis.

Magnetic adsorbent	Composition (%)				
	Fe	O	Si	C	N
MP	61.5	28.0	0.5	–	–
MP@SiO$_2$	5.3	47.6	30.0	–	–
MP@[Chi-SiO$_2$]	4.1	44.7	21.3	22.6	7.3
MP@[Chi-CPTMS(1/4)-SiO$_2$]	6.1	42.5	20.1	23.6	7.8

MP@SiO$_2$. MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$] reached the saturated values at 1 T of external magnetic field. The saturated magnetizations were decreased in the order of MP, MP@SiO$_2$. MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$], due to increase in the content of non-magnetic matters including the silica layer, chitosan, and CPTMS, which is in agreement with the investigations reported by Lei et al. [39], Zhang et al. [29], Sakti et al. [41] and Nuryono et al. [42]. Although MP@[Chi-CPTMS(1/4)SiO$_2$] had the lowest saturated magnetization, it can be easily separated from the solution with an external magnet.

SEM images of MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$] are presented in Fig. 12. Both magnetic adsorbents were irregular in shape and there is no significant difference in the morphology. Table 4 summarizes the surface compositions of MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$] estimated by EDX analysis. Through the modification of MP with the silica layer, the surface composition of Fe was significantly decreased and instead that of Si was increased, indicating that the surface of MP was almost completely covered with the silica layer. With the further modifications with chitosan and CPTMS, both carbon and nitrogen were detected. There was no significant difference in the compositions of carbon and nitrogen between MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)SiO$_2$], suggesting that the amount of chitosan exposed on the surface was almost constant. In other words, it is presumable that CPTMS was present under the chitosan layer, as proposed in Fig. 2(b).

Fig. 13 shows IR spectra of MP@SiO$_2$, MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)-SiO$_2$]. MP@SiO$_2$ gives the IR bands due to Fe–O (at 555 cm^{-1}), Si–O–Si (at 797 and 1088 cm^{-1}), physically adsorbed water (at 1643 cm^{-1}) and hydrogen bonded silanol overlapping with N–H groups (at 3449 cm^{-1}). On the spectra of MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS(1/4)-SiO$_2$], the IR bands assignable to stretching vibrations of C–H from chitosan and CPTMS were observed at around 2800-3000 cm^{-1}. Unfortunately, the IR spectrum of MP@[Chi-CPTMS(1/4)-SiO$_2$] was quite similar to that of MP@[Chi-SiO$_2$] and the IR band corresponding to deformation vibration of secondary amines at around 1550 cm^{-1} is observed. That is probably due to the small absorption coefficient for deformation vibration of secondary amines.
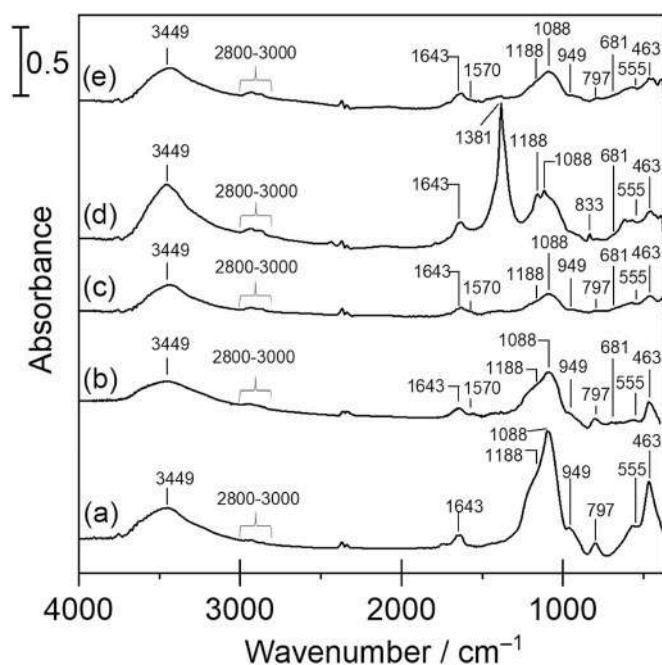
Fig. 13. IR spectra of (a) MP@SiO$_2$, (b) MP@[Chi-SiO$_2$] and MP@[Chi-CPTMS (1/4)-SiO$_2$] (c) before adsorption, (d) after adsorption and (e) after desorption of Au(III). The spectra were measured with a KBr method.

3.5. Characterization of MP@[Chi-CPTMS(1/4)-SiO$_2$] after adsorption and desorption of Au(III)

MP@[Chi-CPTMS(1/4)-SiO$_2$] after the adsorption and desorption of Au(III) was investigated by using XRD (Fig. 9d and e), SEM (Fig. 12c and d), and FTIR (Fig. 13d and e). After the adsorption of Au(III) (Fig. 9d), new diffraction lines due to cubic Au appeared at $2\theta = 38.31$; 45.58 and 66.46° which assignable to (111), (200), and (220), respectively. Meanwhile, the additional diffraction lines marked by asterisk may be caused by the crystallization of unoxidized Au(III) complexes [43,44]. After the treatment of the spent MP@[Chi-CPTMS(1/4)-SiO$_2$] in thiourea solution in 0.1 M HCl solution to facilitate the desorption, the diffraction lines of Au disappeared (Fig. 9e), indicating that the successful desorption of Au. However, the intensity of diffraction lines due to Fe$_3$O$_4$ were also decreased with the treatments, while no change in the diffraction angles were observed, suggesting that the acidic condition of the treatment negatively affects the crystallinity of the magnetite core. The changes in the shape and size of particles through adsorption and desorption of Au(III) were also observed on the SEM images (Fig. 12c and d).

As shown in Fig. 13d, e, a new sharp band appeared at 1381 cm^{-1} on the IR spectrum of MP@[Chi-CPTMS(1/4)-SiO$_2$] after the adsorption of Au(III) and was completely diminished after the treatment for the desorption. This band corresponds to deformation vibration of C–H, which directly bonds with amino group of chitosan. This new band may be caused by change in the environment around C–H moiety due to the adsorption of Au(III). It is noted that the spectrum after the desorption (Fig. 13e) was almost identical to that of pristine MP@[Chi-CPTMS(1/4)-SiO$_2$] (Fig. 13c), indicating that adsorption-desorption of Au(III) did not cause damage to the functional groups on MP@[Chi-CPTMS(1/4)-SiO$_2$].

4. Conclusions

In the present study, we synthesized the magnetic adsorbent that the iron sand magnetic particles, which was prepared from natural iron sand, were modified with chitosan-silica matrix through a sol-gel

process using CPTMS as a coupling agent. Since the magnetic particles were almost completely covered with the silica layer and chitosan was tightly held on the silica layer through CPTMS, MP@[Chi-CPTMS(1/4)-SiO$_2$] and MP@[Chi-CPTMS(3/4)-SiO$_2$] were highly stable even in acidic solution with pH 3 or lower. Since chlorine of CPTMS strongly interacted or formed a covalent bond with amino group in chitosan, which acted as adsorption site for Au(III) ion, excess CPTMS decreased the adsorption site and significantly lowered the adsorption capacity for Au(III) ion. In terms of stability and adsorption capacity, the best of magnetic adsorbents studied was MP@[Chi-CPTMS(1/4)-SiO$_2$], which exhibited the maximum adsorption capacity of 112 mg g^{-1} for Au(III) ion for the solution with pH 5. The adsorbent showed high selectivity of Au(III) adsorption in a solution containing Cu(II) and Zn(II) in addition to Au(III) and was reusable for two times keeping high selectivity of Au (III) adsorption without fatal decline in the adsorption performance.

CRediT authorship contribution statement

Nuryono Nuryono: Conceptualization, Formal analysis, Supervision, Writing - review & editing, Project administration, Resources. **Dikki Miswanda:** Funding acquisition, Investigation, Writing - original draft. **Satya Candra Wibawa Sakti:** Formal analysis, Writing - review & editing. **Bambang Rusdiarso:** Conceptualization, Supervision. **Philip Anggo Krisbiantoro:** Funding acquisition, Visualization, Formal analysis. **Nastiti Utami:** Validation, Investigation, Funding acquisition. **Ryoichi Otomo:** Writing - review & editing. **Yuichi Kamiya:** Conceptualization, Formal analysis, 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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