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Functionalization of Silica Coated on Iron Sand Magnetic Material with Diethylenetriamine

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Diethylenetriamine (DETA) functionalized silica coated on magnetic material of iron sand (MM@SiO_2–DETA) has been synthesized by sol–gel method. Synthesis was carried out by coating magnetic material of iron sand as the core with diethylenetriamine–modified silica using sodium silicate solution and N^1–(3–trimethoxysylilpropyl)diethylenetriamine (TMPSDETA) as silica and diethylenetriamine group sources, respectively. Several variations of mole ratio of silica to DETA at a constant weight of magnetic material were examined to evaluate the effect of the coating agent amount on the properties of MM@SiO_2–DETA. MM@SiO_2–DETA was characterized with Fourier transform infrared spectrophotometer, X-ray diffraction, scanning electron microscope with energy dispersive spectroscope (SEM–EDX), vibrating sample magnetometer and thermal gravimetric analysis. Stability test of product toward acidic solution and the effect of mole ratio of SiO_2 and DETA on adsorption of Au(III) also evaluated. The characterization results indicated that SiO_2 and DETA groups were successfully attached to the surface of magnetic material to form MM@SiO_2–DETA. Characteristic bands of the vibration of propyl and amino groups derived from DETA; indicating that DETA was successfully reacted with MM@SiO_2. Coating of magnetic material with SiO_2 exhibits the decrease in M_s up to 38.2 emu/g and 23.5 emu/g after coating with SiO_2–DETA. Thermalgravimetric analysis indicate thermal stability of the resulted product of MM@SiO_2–DETA (1:1) up to 350 °C. Dissolution by acid solution can be diminished by coating magnetic material with silica. Gold(III) adsorption capacity of MM@SiO_2–DETA (1:0.5), MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2) are found to be higher than 92 %.

Keywords: Diethylenetriamine, Silica, Iron sand.

INTRODUCTION

Several treatment processes such as reverse osmosis, ion exchange, chemical precipitation and adsorption are currently used in gold removal and recovery gold from wastewater for recycling and reuse [1-5]. Among these methods, the adsorption has a high potential to be developed further for its low cost, easy to operate, relatively simple for maintaining. Furthermore, it has high loading capacity and possibly to apply at a low concentration of adsorbent [2,5,6].

Numerous materials have been investigated as gold adsorbents such as natural bio–sorbents (*e.g.* algae, bacteria and yeast) [7], synthetic materials including mesoporous adsorbents [6], chitosan derivatives [8] and graphitized carbon black [9] as well as modified silica [10-12]. Silica is widely used as an adsorbent due to its excellent thermal and mechanical stability, easily dispersed in a liquid medium, it has large surface area and well–modified surface properties. In addition, this material contains silanol and siloxane groups on its surface which can be easily modified with various functional groups such as amino and thiol [13,14]. Previous researchers have used various functional groups to modify silica for adsorption of Au(III) such as (3–[3–(methoxycarbonyl)benzylidene]hydrazinyl) benzoic acid (MBHB) [15], 3–aminopropyltrimethoxysilane (APTMS) [13], 3–aminopropyl, N–[2–aminoethyl]–3–aminopropyl and 3–mercaptopropyl [10] and diethylenetriaminemethylenphosphonic acid [16]. As one of the promising adsorbent, silica possesses excellent adsorption ability, but the difficulty of separating adsorbent from solution after process limits the application. Therefore, magnetic material of iron oxides such as magnetite (Fe_3O_4), has recently gained much attention for gold adsorption. However, uncoated magnetite is highly susceptible to the oxidation when it is exposed to the atmosphere and leaching under acidic condition [17]. Thus, coating magnetite with silica can cover the surface of magnetite to form Fe_3O_4@SiO_2 [18].

It is important to note that previous studies have used synthetic magnetic material of iron oxide coated with functional group modified silica. Sources of magnetic material are able to be derived either from the precursor $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ [2,19,20], $Fe(NO_3)_3{\cdot}9H_2O$ [21] or $FeSO_4{\cdot}7H_2O$ and $Fe_2(SO_4)_3{\cdot}nH_2O$ [22]. Several chemical methods can be used

to synthesize magnetic material of iron oxides, including co–precipitation reactions occur in the mixture solution of Fe^{2+} and Fe^{3+}, thermal decomposition of the organic iron precursor, solvothermal, hydrothermal and microemulsion methods [23,24]. Such methods are suitable for synthesis of α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4 with different proportions by controlling the reaction conditions. However, the methods have disadvantages such as the difficultness to avoid nucleation during reaction, requiring relatively high temperatures, possessing complicated procedures, relatively slow kinetics at low temperature condition and the use of multiple reagents.

Only few studies on the use of natural magnetic material have been reported. High magnetite ingredients in iron sands are certainly encouraging the utilization of iron sand for magnetic material. For this, iron sand has high economic value once it is processed as magnetic materials. The process does not need a large–scale mining, that the mining and processing can be done selectively [25,26].

The immobilization of functional groups on the silica surface is generally prepared through several processes, in which the silica gel is reacted with a compound containing a functional group in the medium of water–free toluene [2,16,19]. Modification of silica is typically accomplished through silanization reaction, yet requires long and tedious procedure through heating process. To overcome this problem, several studies with a simple technique of sol–gel process for modification of silica with functional groups have been reported [19,27-29].

The present study reports a simple process of coating iron sand magnetic material (MM) with diethylenetriamine (DETA) modified silica through a one pot reaction and the adsorption characteristics of Au(III) on the resulted adsorbent.

EXPERIMENTAL

FTIR spectra of the products were recorded with Fourier transform infrared spectrophotometer (FTIR–PRESTIGE 21) using KBr pellets. The XRD data was acquired by X–ray diffractometer (Shimadzu XRD 6100). The magnetic property of the materials was analyzed by vibrating sample magnetometer (VSM type OXVORD VSM 1.2H). Elemental analysis of the resulted adsorbent was determined with SEM–EDX (JSM–6510). The thermal analysis was performed using a NETZSCH STA 449F1 employing heating at rate 10 °C min^{-1} in the air atmosphere. The concentration of Au(III) in the adsorption experiment was analyzed with using flame atomic absorption spectroscopy (FAAS, Analytic Jena ContrAA 300).

N^1–(3–Trimethoxysylilpropyl)diethylentriamine (TMPSDETA), sodium silicate solution (Na_2SiO_3) with the weight percentage of SiO_2 25.5–28.5 % and Na_2O 7.5–8.5 % were obtained from Sigma–Aldrich Corp. Ltd (Germany). Hydrochloric acid (HCl), sodium hydroxide (NaOH), chloroauric acid standard solution ($HAuCl_4$) 1000 mg/L of Au(III) were purchased from Merck Co. Inc (Germany). All chemicals were of analytical grade and used without further treatment. The magnetic material was obtained from iron sand collected from Bugel Beach, Kulonprogo, Yogyakarta, Indonesia. Magnetic material was separated from iron sand with a permanent magnet and grounded with mortal prior to sieve a 200 mesh in size. Magnetic material with size > 200 mesh was washed with distilled water and dried in an oven at 95 °C for 18 h, followed by refluxing at 75–80 °C using 4 M NaOH solution for 2 h. The magnetic material was washed using distilled water until the washing water pH was 7.0 and dried in an oven at 95 °C for 18 h [26].

Synthesis of MM@SiO_2–DETA: About 0.5 g of magnetic material dispersed in 1 mL of HCl solution 1 M was added a certain volume of sodium silicate solution and TMPSDETA. The mole ratio of SiO_2 in sodium silicate solution to TMPSDETA were varied as presented in Table-1. The mixture was then added drop–wise HCl 1 M solution until the solution pH reached ≈ 7.0. The resulted precipitate was ultrasonificated for 15 min and kept overnight at a room temperature to form gel. The gel was dried at 80 °C for 5 h, grounded with a mortal and washed with deionized water until pH » 7.0. The resulted material was separated with an external magnet and dried at 80 °C for 5 h.

TABLE-1
VOLUME AND MOLE RATIO OF SILICA TO DETA FOR PREPARATION OF MM@ SiO_2–DETA

Code of product	Volume/amount of coating agent	
	Na_2SiO_3 (mL/mol SiO_2)	TMSPDETA (mL/mol DETA)
MM@SiO_2–DETA (0:1)	0.00/0.00	0.74/2.89
MM@SiO_2–DETA (1:0)	2.00/2.89	0.00/0.00
MM@SiO_2–DETA (1:0.5)	2.00/2.89	0.37/1.44
MM@SiO_2–DETA (1:1)	2.00/2.89	0.74/2.89
MM@SiO_2–DETA (1:2)	2.00/2.89	1.48/5.75

The weight fraction (wf) of coated material was calculated using eqn. 1:

$$wf\ (\%) = \left(1 - \frac{w_o}{w_t}\right) \times 100 \quad (1)$$

where wf (%) is weight fraction of coated material, w_o (g) and w_t (g) are initial and final weight of coated material, respectively.

Stability test of product toward acidic solution: Product sample was added with 30 mL of HCl 1 M solution, shaken for 2 h and kept in a room temperature for (1, 2, 7 and 11 day). The substrate collected in various interval days (1, 2, 7 and 11 day) 3 mL each and the content of dissolved iron was analyzed with FAAS.

Effect of mole ratio of SiO_2 and DETA on adsorption of Au(III): Adsorption from aqueous solution was conducted in a batch system. The amount of adsorbent (0.02 g) was mixed with 50 mg/L of $AuCl_4^-$ in buffer solution pH 2, the suspension was shaken at a room temperature for 2 h. After the adsorption reached an equilibrium, the bottle was placed on a permanent magnet to separate adsorbent from the aqueous solution, then the supernatant was collected and the concentration of gold was analyzed with FAAS.

RESULTS AND DISCUSSION

Characteristics of MM@SiO_2–DETA: In this work, several variations of mole ratio of silica to DETA at a constant weight of magnetic material were examined to evaluate the effect

of the coating agent amount on the properties of MM@SiO_2–DETA. Table-2 shows the weight of magnetic material coated with silica-DETA before and after washing with deionized water and the fraction of coated material. Coating of magnetic material with silica and DETA increases the weight with the order MM@SiO_2–DETA (0:1), MM@SiO_2–DETA (1:0), MM@SiO_2–DETA (1:0.5), MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2). The weight of adsorbent decreases after washing with deionized water due to dissolution of sodium chloride from the reaction between sodium silicate and HCl. This by–product may be trapped in the coated magnetic material as an impurity. By using sodium silicate as the silica source, washing the precipitate is an important step to find the coated magnetite with free of unwanted byproduct [19].

TABLE-2
WEIGHT OF MAGNETIC MATERIAL COATED WITH SILICA–DETA BEFORE AND AFTER WASHING WITH DEIONIZED WATER AND FRACTION OF COATED MATERIAL

Product	Weight (g)		Weight fraction of coated material (%)
	Before washing	After washing	
MM@SiO_2–DETA (0:1)	1.06	0.78	35.89
MM@SiO_2–DETA (1:0)	1.04	0.78	35.89
MM@SiO_2–DETA (1:0.5)	1.36	1.10	54.54
MM@SiO_2–DETA (1:1)	1.56	1.18	57.63
MM@SiO_2–DETA (1:2)	2.09	1.38	63.77

Stability of coated magnetic material in acidic medium: The stability of synthesized product was tested against acid, since acid generally is used in adsorption and desorption of Au(III). Fig. 1(a) shows the result of dissolution test of magnetic material, MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2) in HCl 1M solution with various contact times (from 1 to 11 days). Iron oxides such as Fe_3O_4 in magnetic material dissolves readily in HCl solution to form Fe^{2+} and Fe^{3+} ions following the equation.

$$Fe_3O_{4(s)} + 8HCl_{(aq)} \longrightarrow 2FeCl_{3(aq)} + FeCl_{2(aq)} + 4H_2O_{(l)}$$

Dissolution by acid solution can be diminished by coating magnetic material with silica, as silica forms shell to protect magnetite core particles [2,19]. Magnetic material was completely dissolved in 1 M solution of HCl forming a yellow solution [Fig. 1(b)], while less Fe^{2+} ion was detected in the supernatant of MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2).

Functional groups: The FTIR spectra of magnetic material, MM@SiO_2–DETA (1:0), MM@SiO_2–DETA (0:1), MM@SiO_2–DETA (1:0.5), MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2) are presented in Fig. 2. In FTIR spectrum of magnetic material [Fig. 2(a)] an absorbance band at 570 cm^{-1}, is observed corresponding to Fe-O vibration. The bands at 1628 and 3448 cm^{-1} are assigned to –OH groups as bending and stretching vibrations, recpectively, from Fe-OH and Si-OH. Bands at 795, 1072 and 950 cm^{-1} of MM@SiO_2–DETA (1:0) spectrum [Fig. 2(b)] correspond to the asymmetry and symmetry stretching vibration of Si-O-Si and bending vibration of Si-O, respectively [16]. The FTIR spectra of MM@SiO_2–DETA (0:1), MM@SiO_2–DETA (1:0.5), MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2) in Fig. 2(c–f) show characteristic bands of the vibration of propyl and (NH_2) amino groups derived from DETA; indicating that DETA was successfully reacted with MM@SiO_2. The presence of the propyl group is identified bands at 1080–1049 cm^{-1} and 1473–1400 cm^{-1} resulted from -C-C- stretching vibration and bending vibration of -CH_2-, respectively. The bands in 2954–2924 cm^{-1} region are associated with asymmetric stretching vibration of C-H from propyl group. Amino groups are identified by bands at 1636 and 1574 cm^{-1} from bending vibration and stretching vibration of -NH_2 and -NH, respectively [14,30]. It can be concluded that the IR spectra support the success of coating EDTA modified silica on magnetic material.

Crystalline structure: Fig. 3 shows XRD patterns of magnetic material, MM@SiO_2 and MM@SiO_2–DETA (1:1). In the XRD pattern of magnetic material [Fig. 3(a)], characteristic peaks at 30.08°, 35.44°, 43.04°, 53.42°, 57.00° and 62.48° are corresponding to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystal planes of the pure magnetite (Fe_3O_4) with a spinal structure (PDF file no 19–0629), except for peak at 2θ = 27.72° which is confirmed to quartz (SiO_2) particles [26,30]. The typical XRD profile of MM@SiO_2 [Fig. 3(b)]

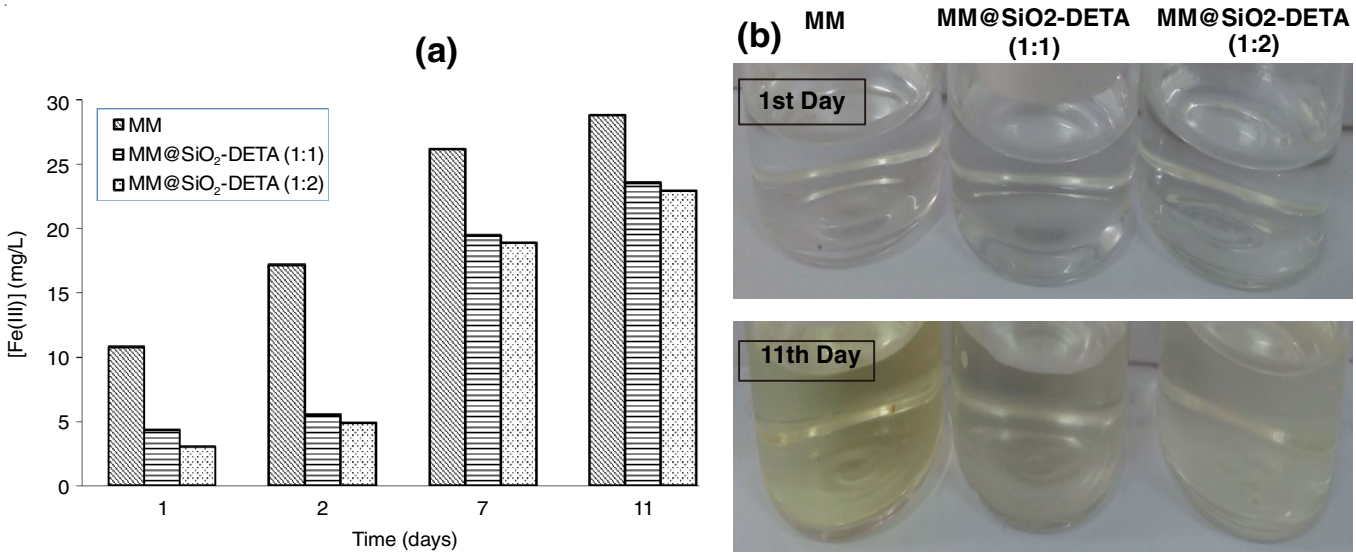

Fig. 1. (a) The amount of Fe dissolved in 1M HCl solution and (b) colour of magnetic material, MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2) supernatant after dissolution

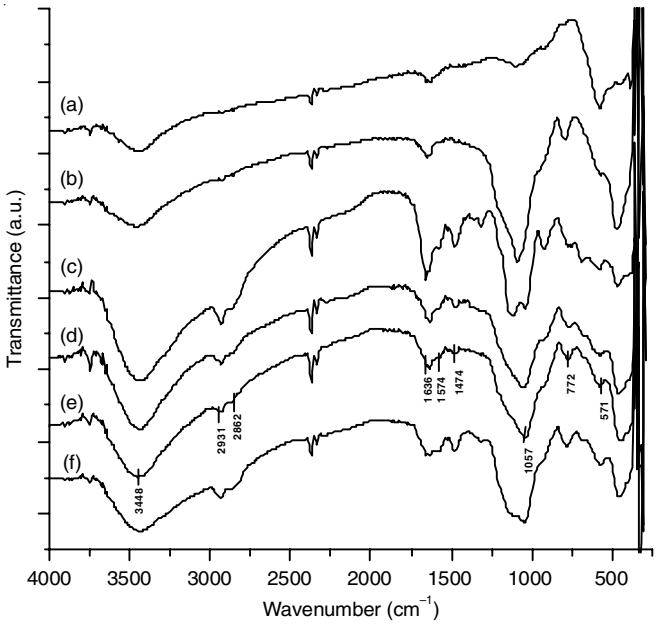

Fig. 2. Infrared spectra of (a) magnetic material, (b) MM@SiO_2–DETA (1:0), (c) MM@SiO_2–DETA (0:1), (d) MM@SiO_2–DETA (1:0.5), (e) MM@SiO_2–DETA (1:1) and (f) MM@SiO_2–DETA (1:2)

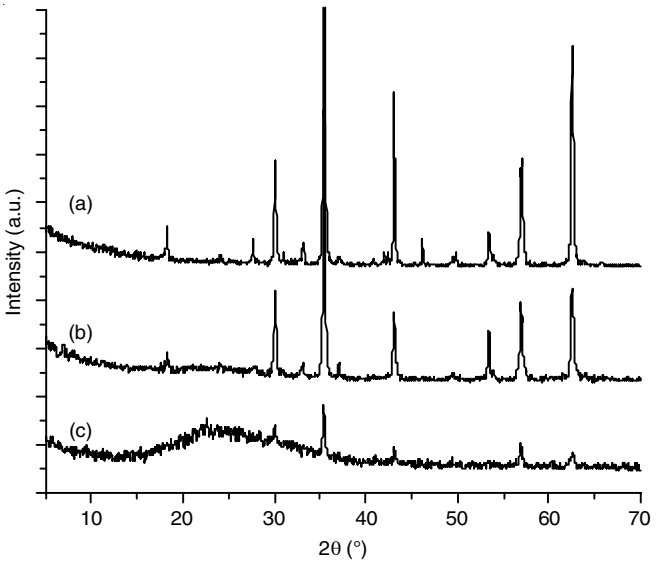

Fig. 3. XRD pattern of (a) magnetic material, (b) MM@SiO_2 and (c) MM@SiO_2–DETA (1:1).

informs that coating magnetic material with silica does not change the peak position, but the intensity of the peaks decreases. Moreover, the XRD pattern of MM@SiO_2–DETA (1:1) [Fig. 3(c)] shows the board peak around 2θ = 20-30° due to the addition of amorphous silica and TMSPDETA on the surface of magnetic material which may cover the crystal particles and lead to the decrease of peak intensity [31].

Magnetization: The magnetic properties of the magnetic material, MM@SiO_2 and MM@SiO_2–DETA (1:1) were measured by VSM and the results are shown in Fig. 4. The mass saturation magnetization (M_s) of magnetic material was found to be 64.0 emu/g. Coating of magnetic material with SiO_2 exhibits the decrease in M_s up to 38.2 emu/g [Fig. 4(b)] and 23.5 emu/g after coating with SiO_2–DETA [Fig. 4(c)]. The reduction of M_s is attributed to the contribution of the non magnetic SiO_2–DETA to the total mass of the particles [29]. Zhang *et al.* [2] have emphasized the reduction of the maximum saturation magnetization from 55.05 to 20.14 emu/g when coating magnetite with thiol–silica. Fig. 4 also shows that all materials produce small curve areas; indicating low energy for magnetization and are classified as soft magnet. This assumption is supported by the low H_c values of the samples. The value of $H_c \neq 0$ for magnetic material, MM@SiO_2 and MM@SiO_2–DETA (1:1) indicates ferrimagnetic properties of the samples [26].

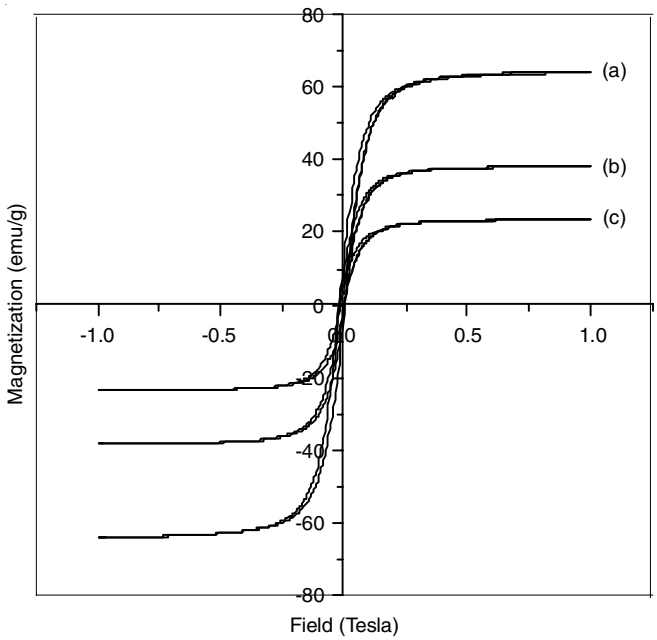

Fig. 4. VSM hysteresis curve of (a) magnetic material, (b) MM@SiO_2 and (c) MM@SiO_2–DETA (1:1)

Morphology and chemical composition: The percentage of distributions of iron, silicon, oxygen, carbon and nitrogen elements in magnetic material, MM@SiO_2 and MM@SiO_2–DETA (1:1) were determined based on EDS data. The SEM images representing the profile of product surfaces and EDS spectra of magnetic material, MM@SiO_2 and MM@SiO_2–DETA (1:1) are given in Fig. 5. The SEM image results show that the MM@SiO_2–DETA (1:1) surface image is not much different from that of MM@SiO_2. The image shows a subtle material surface and a non–uniform or irregular shape. The EDS data of magnetic material, MM@SiO_2 and MM@SiO_2–DETA (1:1) are given in Table-3. The iron, silicon, oxygen, carbon and nitrogen contents in EDS spectra of magnetic material are 66.73, 1.69, 24.88, 4.60 and 2.10 % (w/w), respectively. The EDS spectra of MM@SiO_2 shows the decrease of iron content [12.4 % (w/w)], while the contents of silicon and oxygen increase up to 29.61 % and 45.48 % (w/w), respectively, due to the contribution of SiO_2 in the surface of magnetic material. In Fig 5(c), the EDS spectra of MM@SiO_2–DETA (1:1) show that the nitrogen content significantly increases up to 15.29 % (w/w), while the contents of iron, silicon, oxygen and carbon are 9.54, 19.15, 36.70 and 19.32 % (w/w), respectively. Such results indicate that magnetic material was successfully coated with SiO_2 and DETA.

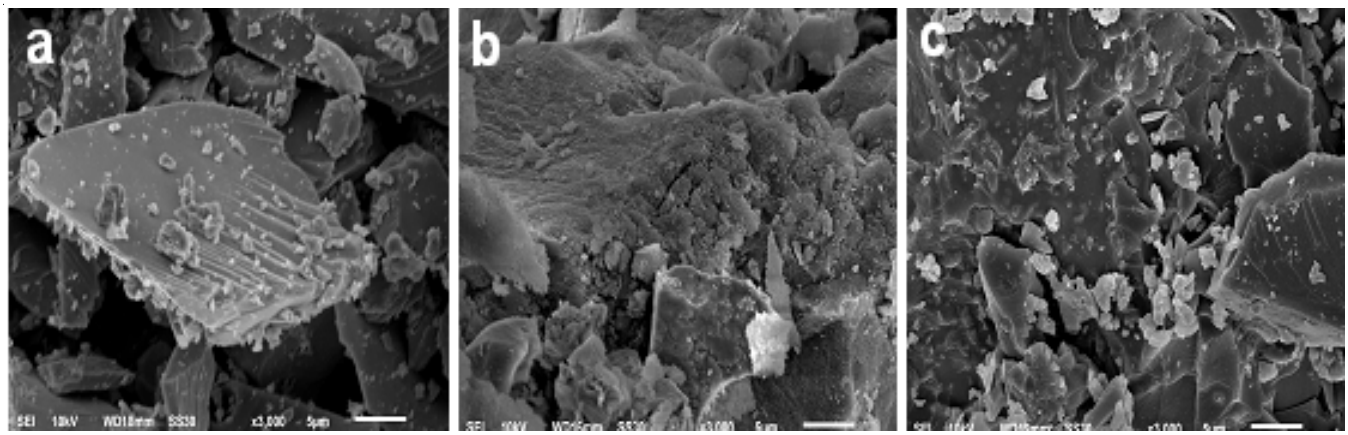

Fig. 5. SEM image of (a) magnetic material, (b) MM@SiO_2 and (c) MM@SiO_2–DETA (1:1)

TABLE-3
EDS DATA OF MAGNETIC MATERIAL, MM@SiO_2 AND MM@SiO_2–DETA (1:1)

Product	Wt %					At %				
	CK	NK	OK	SiK	FeK	CK	NK	OK	SiK	FeK
Magnetic material	4.60	2.10	24.88	1.69	66.73	11.45	4.49	46.51	1.80	35.74
MM@SiO_2	9.19	3.38	45.48	29.61	12.35	14.93	4.70	55.48	20.58	4.32
MM@SiO_2–DETA (1:1)	19.32	15.29	36.70	19.15	9.54	27.51	18.67	39.24	11.66	2.92

Thermalgravimetric analysis: Thermalgravimetric curve reflects the thermal stability of materials and also is used to determine the content of organic functional groups of the sample. Thermalgravimetric curves of MM@SiO_2 and MM@SiO_2–DETA (1:1) shown in Fig. 6. Weight loss at below 210 °C for MM@SiO_2 may be attributed to the physically absorbed water molecules eliminated from the surface of the silica layer. The easy weight loss (4.43 wt %) above 300 to 800 °C is characteristics of the condensation of silanol group bonded to the surface of magnetic material. The TGA curve of MM@SiO_2–DETA (1:1) shows a weight loss (9.14 wt %) from 80 to 280 °C which is associated with the release of water structure. Mass change of 19.92 wt % from 300 to 800 °C apart from water loss events is resulted from the decomposition of the organic moeities of diethylenetriamine groups grafted to the silica surface and the condensation of the remaining silanol group [5,12,32]. These thermalgravimetric curves indicate thermal stability of the resulted product of MM@SiO_2–DETA (1:1) up to 350 °C.

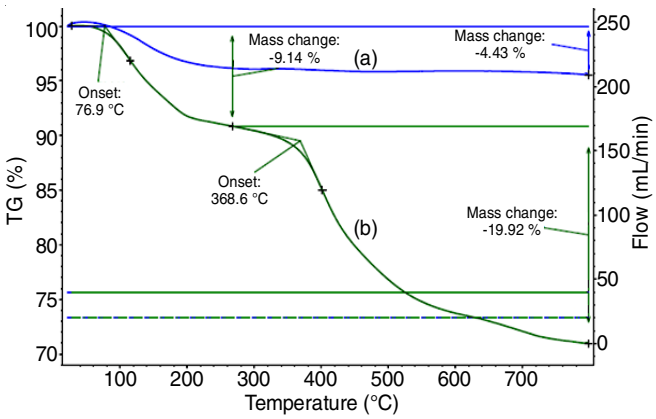

Fig. 6. Thermalgravimetric curves of (a) MM@SiO_2 and (b) MM@SiO_2–DETA (1:1)

Effect of mole ratio of SiO_2 and DETA on adsorption: Fig. 7 shows the effectiveness of Au(III) adsorption on the resulted adsorbents of MM@SiO_2, MM@SiO_2–DETA (0:1), MM@SiO_2–DETA (1:0.5), MM@SiO_2–DETA (1:1), MM@SiO_2–DETA (1:2). The Au(III) adsorption capacity of MM@SiO_2 (18.11 %) is lower than other adsorbents. Although adsorbent of MM@SiO_2–DETA (0:1) shows highest adsorption capacity (97.25 %), this is not chosen as good adsorbent since it is not coated with silica and easily dissolved under acidic condition as explained previously. Furthermore, Au(III) adsorption capacity of MM@SiO_2–DETA (1:0.5), MM@SiO_2–DETA (1:1) and MM@SiO_2–DETA (1:2) are found to be 92.50, 94.68 and 94.46 %, respectively. The heavy metal ion removal mechanism by amine–functionalized adsorbent comprises electrostatic interactions, coordination interactions and ion exchange due to the metal ion complexing capability of amino groups [33,34]. The amino groups of DETA may serve as an active site, thus the adsorption capacity is expected to be higher by increasing the number of amino groups. However, high amino density may lead pore block and limit the mass transfer into the available active sites [21].

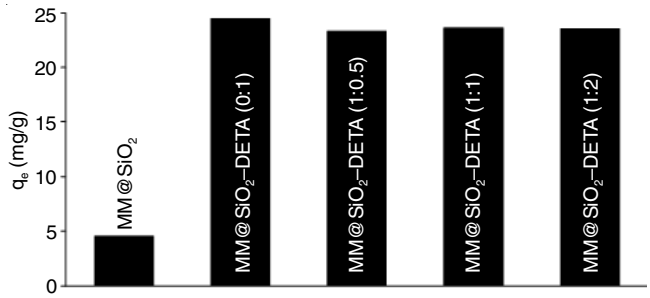

Fig. 7. Au(III) adsorption onto MM@SiO_2, MM@SiO_2–DETA (0:1), MM@SiO_2–DETA (1:0.5), MM@SiO_2–DETA (1:1), MM@SiO_2–DETA (1:2) adsorbents. Experimental conditions: 20 mg adsorbent per 10 mL $[AuCl_4]^-$ 50 mg/L solution, room temperature, contact time 2 h, pH 2

Conclusion

Magnetic material of iron sand coated with diethylenetriamine–functionalized silica (MM@SiO_2–DETA) has been successfully prepared by sol–gel method. The Au(III) adsorption capacity of MM@SiO_2–DETA (1:1) is 94.68 %. MM@SiO_2–DETA is suitable and potential for Au(III) ions recovery due to its low cost and easy to synthesize, good magnetic separation performance, stable under acidic conditions and high adsorption capacity.

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