Indian Journal of Chemical Technology
Vol. 27, September 2020, pp. 387-394

Fabrication of silica-based chitosan biocomposite material from volcanic ash and shrimp husk by sol gel method for adsorbent of cadmium (II) Ions

Lisnawaty Simatupang[1,2], Manihar Situmorang*,[2], Harlem Marpaung[1] & Rikson Siburian[1]

[1]Postgraduate Study Program, Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Sumatera Utara, Jl. Bioteknologi, Kampus USU Padang Bulan, Medan, North Sumatera, 20155, Indonesia

[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Psr. V, Medan, North Sumatera, 20221, Indonesia

*Corresponding author: Manihar Situmorang, Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Negeri Medan, Jl. Willem Iskandar Psr. V, Medan, North Sumatera, 20221, Indonesia,
E-mail: msitumorang@unimed.ac.id

Received 6 May 2019; accepted 3 September 2020

The utilization of volcanic ash and shrimp shell waste into composite material is very interesting to discuss as a strategy to make naturally available materials into valuable, stable and low cost adsorbent. The study is aimed to fabricate the silica-based chitosan biocomposite material from volcanic ash of Sinabung mountain and shrimp husk by sol gel method to be used as an adsorbent. The procedure is performed by converting volcanic ash into silica salt, extracting the chitosan from shrimp skeleton, and the synthesis of the silica-chitosan biocomposite by mixing the silica with chitosan in the aid of bifunctional glutaraldehyde cross-linking agent. The silica-based chitosan composite is successfully prepared from the mixture of 20 mL 58% (v/v) Na_2SiO_3 with 2% (w/v) chitosan to obtain biocomposite material (SChC1). A rapid and simple method to bind the silica with chitosan is achieved. The resulting biocomposite is amorphous, in the form of small crystals, a rough surface with a large pore area between $2\theta = 20\text{-}24°$. Adsorption capacity of the biocomposite material has been evaluated, where it has the capability to bind cadmium ion due to the presence of amine group in the material surface. The prepared material of silica-chitosan biocomposite has the potential to be used as an adsorbent.

Keywords: Sol-gel method, Silica-chitosan biocomposite, Volcanic ash, Adsorbent, Heavy metal

The use of silica-chitosan composite become promising material for its favour in the functional group that can be modified for different applications in analytical methods. Biocomposite is a valuable material for practical application in Analytical Chemistry due to its biocompatibility and biodegradability, strong bio-adhesivity and film-forming ability, and excellent reusability[1]. Various types of biocomposite materials have been developed and applied for many purposes[2-4]. The application of biocomposite for adsorbent materials to remove heavy metals has been reported[5]. The biocomposite material has also been applied for removing pollutant materials such as cation, anion, dyes, organic compounds, proteins, and heavy metals[6]. The fabrication of composite by utilizing naturally available materials is very challenging to obtain valuable, stable and low cost biocomposite material for adsorbent. One of the abundant raw materials in North Sumatera is volcanic ash that can be utilized as a valuable silica-based composite material.

The eruption of Mount Sinabungin Karo Distric, North Sumatera Indonesia 2013-2018, where many villages are covered with volcanic ash that demolished local plants, and the abundant of the ash becomes a problem for horticultural agriculture in the impact areas[7-9]. The locally available geological ash which has main content of silica (SiO_2) needs to be utilized to become a valuable material.

Some of the very potential properties of the silica such as acid resistance, very strong mechanical properties, large porosity, heat resistance, and resistance to microbial attack make it potential for the manufacture of low cost silica-based composite materials to be applied for many products[10,11]. Previous study has showed that the synthesized silica based material obtained from volcanic ash has successfully produced silica material that has potential to be used as an adsorbent[12]. However, its low surface ability to interact with the target ions required the silica to be modified with organic material such as chitosan to enable the composite material to become an effective adsorbent and other purposes[13,14].

Chitosan is a natural polycationic polysaccharide considered to be an important material to be combined with silica in the preparation of biocomposite material[15–17]. Naturally available organic material of shrimp shell waste can be used as the source of the chitosan. The chitosan with good biocompatibility, high adhesion to the surface, low toxicity and structural variability with amine functional group is a good substance to be used in many applications, including the adsorbents[18–20]. The presence of functional amine group in biomaterial is very important to be employed in various applications such as immobilization of enzyme[21–24], and therefore the chitosan with the amine group can be employed for many purposes, including the sensor and biosensor[25–27]. The physical and chemical properties of chitosan with amino and hydroxyl make it compatible in the preparation of biodegradable silica-chitosan composite for various applications[28]. Although the chitosan contains high amine and hydroxyl groups, it does not have specific selectivity for certain ions such as complex pollutants in water or wastewater[29,30]. The chitosan without modification has low mechanical strength and low solubility in acidic medium. The amine group on chitosan in acid solution causes protonated chitosan. Therefore, modification is needed to optimise the compatibility of the chitosan for further applications.

Sol-gel process is assigned to be a good strategy in the preparation of silica-chitosan composite[31]. The sol-gel method has successfully been used for the composite systems of inorganic–organic biomaterials[32,33]. The reaction is proceeded in the presence of polymeric organic molecule containing functional groups that can immobilised inorganic compounds. Preparation of silica-chitosan composite material has also been carried out in the presence of tetraethoxysilane as precursor of SiO_2[34]. Formation of composite nanomaterial by sol-gel method with intention to modify the silica surface has also been reported[35,36]. The synthesis with this technique is easy to perform, the raw material is cheap, and the yield is rich with multi functional groups[37]. Sol-gel method provides many advantages: the binding process taking place simultaneously, the reaction condition can be performed at room temperature, the procedure is simple, the end product is high in purity, homogeneous, uniform, and small in size[13]. This method is assigned to be effective in the preparation of silica-based biocomposite materials because the combinations of the hardness properties of the silica and the functional group from chitosan are utilized. The study is aimed to fabricate a silica-based chitosan biocomposite material from raw material of volcanic ash of Sinabung mountain and shrimp husk skeleton by sol gel method. The characterization of the biocomposite has been performed, and the potential application of the composite as an adsorbent material to remove heavy metals such as Cadmium ion was also demonstrated.

Experimental Section

Chemical and reagents

Reagent grades of HNO_3, NaOH, HCl, CH_3COOH, ethanol, $CdCl_2$, and glutaraldehyde 25% were obtained from E-Merck and used without purification. All chemicals were dissolved in Milli-Q water. The volcanic ash containing silica was obtained from the eruption area of Mount Sinabung at Brastepu village, Kabanjahe, North Sumatera, Indonesia. The chitosan was prepared from Lobster shrimp husk that was collected from shrimp waste at Percut Sei Tuan, Deliserdang, North Sumatera, Indonesia.

Apparatus

Sample preparation was carried out by using an oven, furnace, sieve (200 mesh), magnetic stirrer, hot plate, ultrasonic (Braunsonic), desiccator, solid-phase extraction column, glass ware and plastic apparatus. The measurements was made by using a Fourier Transform Infra-Red (FTIR) Bruker spectrometer equipped with a Digitech detector (Shimadzu), X-Ray Fluorescence Spectrometer (XRF) (Perkin Elmer 3110), Rigaku ZSX X-Ray Diffraction (XRD) (Shimadzu XRD 6000), Atomic Adsorption Spectrophotometry (AAS) (Z-2000 series), Scanning Electron Microscopy Electron Dispersive X-ray (SEM-EDS) (Zeiss type EPOMH 10 Zss), Gas Sorption Analyser (GSA) with NOVA Quantachrome instruments version 2.2.

Procedures

The procedures in the fabrication of biocomposite are consisted of sample preparation of silica from volcanic ash, extraction of chitosan from shrimp skin, preparation of silica-based chitosan composite, and characterization of the composite followed the procedures explained earlier[13]. The experiment for testing of adsorbent capacity toward heavy metals is also carried out by using modifed procedures explained in the references[38,39].

Preparation of silicate from volcanic ash

The preparation of silicate from volcanic ash was carried out by soaking volcanic ash (20 g) into 120 mL 6M HCl for 24 h, followed by dried the material in an oven (120°C for 6 h), and the weight of the crude product was recorded. The crude was then destructed by using 156 mL 4M of NaOH at the furnace (500°C and 30 min) until the viscous obtained, followed by addition of 200 mL water and let the solution to settle for 24 h. The concentration of sodium silicate (Na_2SiO_3) in the solution has been analyzed using Atomic Absorption Spectroscopy (AAS), obtained 58% (v/v) Na_2SiO_3. The solution was then filtered to produce sodium silicate as silicate raw material.

Extraction of chitosan from shrimp husk

Preparation of the chitosan from shrimp skin skeleton was conducted by cleaning the Lobster shrimp husk, followed by washing, drying, and grinding raw material shrimp shells into powder. Extraction of chitosan from the raw material was performed by using of a 3.5% NaOH solution with a ratio of 1:10 (w/v) at 65°C for 2 h to form chitosan crude, and the procedures are followed by the deproteinase and demineralization process by using of 1N HCl solution with the ratio was kept at 1:15 (w/v) for 30 min at room temperature. The extracted chitosan was then reacted with 60% (w/v) NaOH solution at a ratio of 1:10 (w/v) at 125°C for 2 h. The mixture solution was then cooled, filtered, washed to neutral *p*H condition, and left to dry under sunlight. The chitosan obtained from this procedure was then used as a raw material for the preparation of silica-chitosan biocomposite.

Fabrication of silica-based chitosan biocomposite

The fabrication of silica-based chitosan biocomposite was performed by mixing of sodium silicate with chitosan in a plastic container, and the synthesis was completed by addition of glutaraldehyde crosslinking agent. Various concentration of chitosan solution was prepared by successive addition of (2, 3, 4, and 5) g chitosan into flask containing of 100 mL of acetic acid (2% v/v), and the mixture was then stirred for 1 hour to form (2%, 3%, 4% and 5%) chitosan solutions, followed by addition of 1 mL glutaraldehyde solution (5%) and stirred vigorously for 5 min. A mixture of chitosan and glutaraldehyde solution is then poured into a 20 mL sodium silicate solution under constant stirring in a magnetic stirrer, followed by neutralization by drops addition of 3M HCl until the was *p*H 7.0. The immobilization proceeded overnight to form silica-chitosan gel. The gel was then filtered, washed with MQ-water, dried at 70°C under vacuum condition, and the dry powder is then sieved with a 200 mesh sieve. The end product is named as silica-based chitosan biocomposite material. The biocomposites were labeled based on the composition of chitosan made from 20 mL of silica with (2-5%) chitosan, namely SChC1 for 2%, SChC2 for 3%, SChC3 for 4%, and SChC4 for 5% chitosan, respectively.

Characterization of the silica-based chitosan biocomposite material

The characterization of the biocomposite material was carried out by using of XRD, FTIR and SEM. The X-ray diffractometer was used to collect the XRD data at room temperature by using copper Kα radiation, and the experimental condition was kept at 40 kV and 30 MA, the scanning rate was maintained of 2° min^{-1} in range 2θ from 7° to 70°. The FTIR spectra for the sample was run by using of KBr pellet, scanned in transmission mode with 2 and 4 cm^{-1} resolution at the range of 4000 to 500 cm^{-1}. Characterization for the surface morphology of the biocomposite material was obtained by using a SEM. Specific surface area, pore radius and pore volume was observed by using GSA, and data analysis was collected by using BET method. Silica-based chitosan biocomposite (0.05-0.2 g) was degassed (100°C, 3 h) in a GSA, followed by weighing and collecting the BET data. The adsorption-desorption isotherm of the biocomposite was measured at 77 K, that was a plot from volume (cc/g) *vs* relative pressure (P/P0).

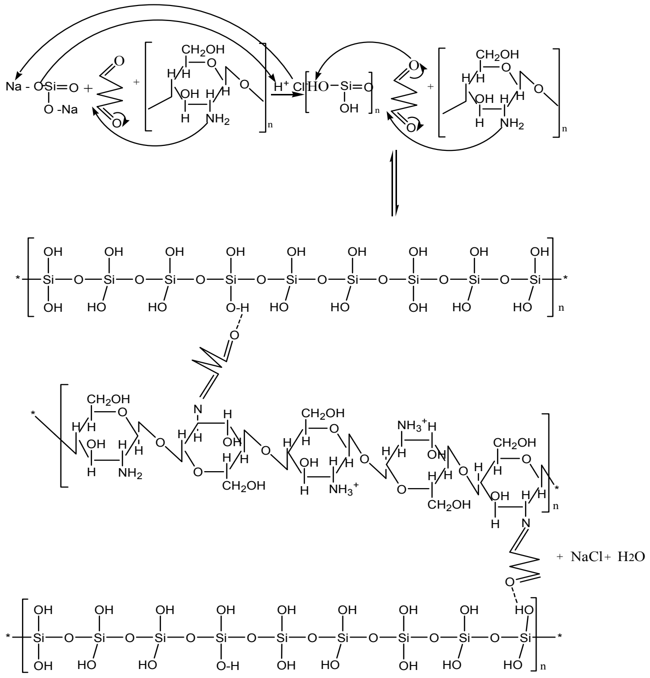
Adsorption capacity of silica-based chitosan biocomposite to Cd(II)Ion

Adsorption capacity of the silica-based chitosan biocomposites (SChC1, SChC2, SChC3 and SChC4) toward heavy metal ion was studied in solid-phase extraction method. The biocomposite (0.5 g) at different compositions were put into dry columns, followed by addition of 10 mL MQ-water and homogenized at neutral condition (*p*H 6.0). A solution of 24 ppm Cd^{2+} was loaded into the column at flow rate 4 mL/min, and the effluent (60 mL) is collected every 15 min., and the remaining Cd(II) ion in the effluent was determined by AAS at λ228.8 nm.

Results and Discussion

Formation of silica-based chitosan biocomposite Material

The silica-based chitosan biocomposite material has successfully been prepared from the immobilization reaction of Na_2SiO_3 (20 mL) with (2-5 %) chitosan by sol-gel method. The chitosan has covalently bounded to the silica surface that was facilitated by the interaction of the protonated amino groups in the organic polymer with the dissociated of the hydroxyl groups available in the silica backbone[40]. The reaction mechanism of the formation of silica-chitosan biocomposite is presented in equation (1).



...(1)

The interaction between the precursor of Na_2SiO_3 and the chitosan has bind together to form a silica-chitosan composite. Immobilisation reaction has successfully bound the silica and the chitosan to form silica-chitosan biocomposite material. The end product of the silica-chitosan biocomposite material is white crystals, and the weight of the crystal varies depending on the variation amount of the added chitosan in the batch reaction. The weight of the resulted biocomposites materials at different treatment conditions is summarised in Table 1. The results revealed that the weight of the biocomposite material increased significantly as increasing the amount of the chitosan immobilised onto the silica based material. The silica-based chitosan biocomposites are labelled successively as SChC1, SChC2, SChC3 and SChC4 depend on the amount of bounded chitosan in the composite materials.

Characterization of silica-based chitosan biocomposite material

The covalent binding between the chitosan and the silica in the immobilization process has been evaluated from the FTIR spectra in the range of 400-4000 cm^{-1} as presented in Fig. 1. It is accertained from the spectra that the mesoporous biocomposite material was containing of amine functional group resulted from the immobilisation of the organic material onto the silica backbone (Fig. 1c-f) which can be compared to the spectra of pure silica gel (Fig. 1a) and pure chitosan (Fig. 1b). The broad bands spectra observed at 790 and 1070 cm^{-1} correspond to the symmetric Si–O bonds and asymmetric Si–O–Si bonds, and the bands at 1700 and 1550 cm^{-1} in the FTIR spectra correspond to the amino groups in the polymer[38,41]. Furthermore, the bands observed at 1380, 1310, and 1080 cm^{-1} are successively corresponding to the presence of C–O–C, C–O, and CH–OH bonds in the biocomposites[29].

Characterization of the biocomposite material has been carried out and the XRD patterns are presented in Fig. 2. The XRD spectra results showed that the biocomposites (SChC1, SChC2, SChC3 and SChC4)

Table 1 — The properties of the silica-based chitosan biocomposites materials based on the mass, BET data, and the adsorption capacity toward Cd(II) ion.

Starting material and the label of biocomposite materials$^+$	Mass (g)	The BET measurement			Adsorption capacity (mg/g)$^\#$
		Surface area (m^2/g)*	Average pore size (A)*	Total pore volume (cc/g)*	
Silica gel	na	374.994	1.5469×10^1	2.900×10^{-1}	na
SChC1 (20 mL:2%)	0.784	138.509	9.69225×10^1	6.712×10^{-1}	16.16
SChC2 (20 mL:3%)	0.971	76.644	1.31547×10^2	5.041×10^{-1}	13.76
SChC3 (20 mL:4%)	1.066	42.079	1.41445×10^2	2.976×10^{-1}	12.48
SChC4 (20 mL:5%)	1.176	85.021	8.00543×10^1	3.403×10^{-1}	14.93

$^+$Biocomposite material is prepared from 20 mL silica with (2% - 5%) chitosan.
*Calculated by using Brauner, Emmet and Teller (BET) method.
$^\#$ Calculated from the concentration of Cd(II) ion after loading (C_t) compare to the original Cd(II) ion (C_0)

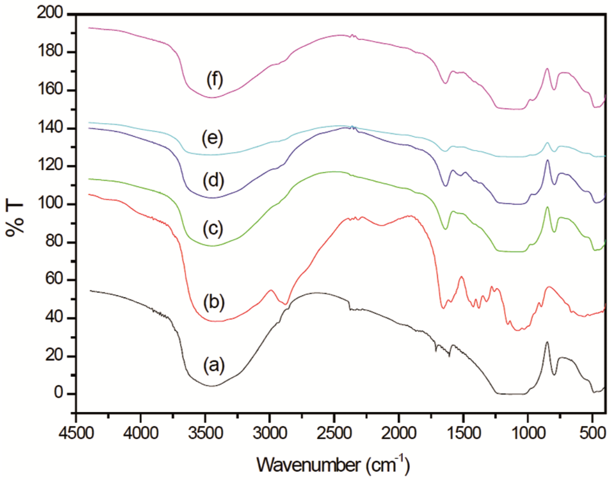


Fig. 1 — The FTIR spectra of: (a) pure silica gel (Sg), (b) pure chitosan (Ch); and for silica-based chitosan biocomposite of: (c) SChC1 (20 mL : 2%), (d) SChC2 (20 mL : 3%), (e) SChC3 (20 mL : 4%), and (f) SChC4 (20 mL : 5%).

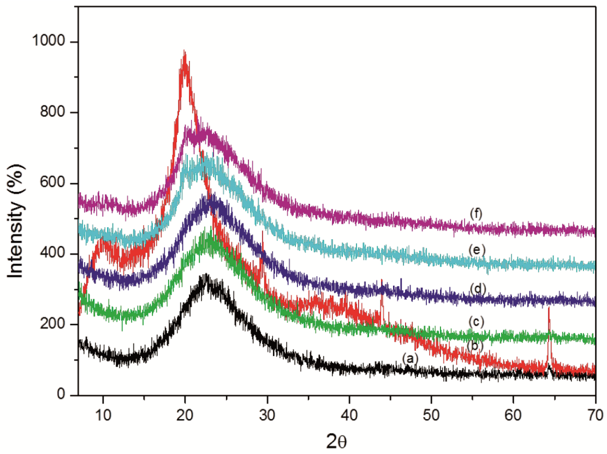


Fig. 2 — The XRD spectra of: (a) pure silica gel (Sg), (b) pure chitosan (Ch); and for silica-based chitosan biocomposite of: (c) SChC1 (20 mL : 2%), (d) SChC2 (20 mL : 3%), (e) SChC3 (20 mL : 4%), and (f) SChC4 (20 mL : 5%).

are tend to be amorphous with small crystalline, the crystal area are obtained between 2θ = 20–24° depends on the amount of immobilised chitosan (Figure 2c-f), which are different to a crystalline structure of the silica at 2θ = 10.1° (Figure 2a) and the chitosan at 2θ = 20.3° (Figure 2b). The XRD spectra revealed that the amount of the chitosan cointained in the biocomposite suppressed the crystallinity pattern. The polymeric chain in the biocomposite material has proven that the silica and the chitosan were bounded well via covalent bonding[42,43].

The SEM images for biocomposites materials and the starting material of silica and chitosan have been compared as presented in Fig. 3. It is revealed that the morphologies of the biocomposite materials (SChC1, SChC2, SChC3 and SChC4) (Fig. 3c-f) are different to those of starting material of silica gel (Fig. 3a) and the chitosan (Fig. 3b). The biocomposites (SChC1) possessed as a non-uniform particle, rough surface with having large pore sice (Fig. 3c), while the biocomposite with very high concentration of chitosan (Fig. 3f) was tend to have uniform particles[44,45]. Addition of chitosan to the silica surface resulted to decrease of the total pore volume of the adsorbent because the chitosan occupies the pores in the silica[29]. Rough surfaces in the biocomposites SChC1 provided more pores to facilitate the adsorbent agent that make it become the best condition to remove heavy metals.

The adsorption/and desorption isotherm for the silica-based chitosan biocomposite has also been evaluated. The adsorption/and desorption isotherm profile for silica-based chitosan biocomposites at various concentration of chitosan in the composite material (SChC1, SChC2, SChC3 and SChC4) have been obtained as presented in Fig. 4. The highest adsorption/and desorption profile have been obtained at biocomposites SChC1 and the lowest is found at biocomposite SChC4. It is seen from the results that the adsorption/and desorption of the biocomposites are significantly influenced by the amount of immobilised chitosan that are bounded in the composite materials[46,47]. The adsorption/and desorption profile has confirmed that the composite material is assigned to be a mesoporous particle[48].

Properties of silica-based chitosan biocomposite material

The biocomposite with variation concentration of immobilised chitosan onto silica has been evaluated by SAS method followed by BET analysis toward heavy metal. The properties of the developed biocomposites based on the mass, BET measurements, and the adsorption capacity is summarised in Table 1. The mass of biocomposite increased significantly with addition of higher concentration of the chitosan. This reveals that immobilisation the chitosan has completely immobilised to the silica main body. It is observed that more chitosan bounded onto the silica surface resulted to decrease of total pore volume of adsorbent, this might be due to the occupation of the pores of silica by the chitosan. The BET analysis has showed that the surface area of the biocomposite varies depending on the amount of chitosan added in the biocomposite material. The surface area for the biocomposites are smaller compare to the surface area

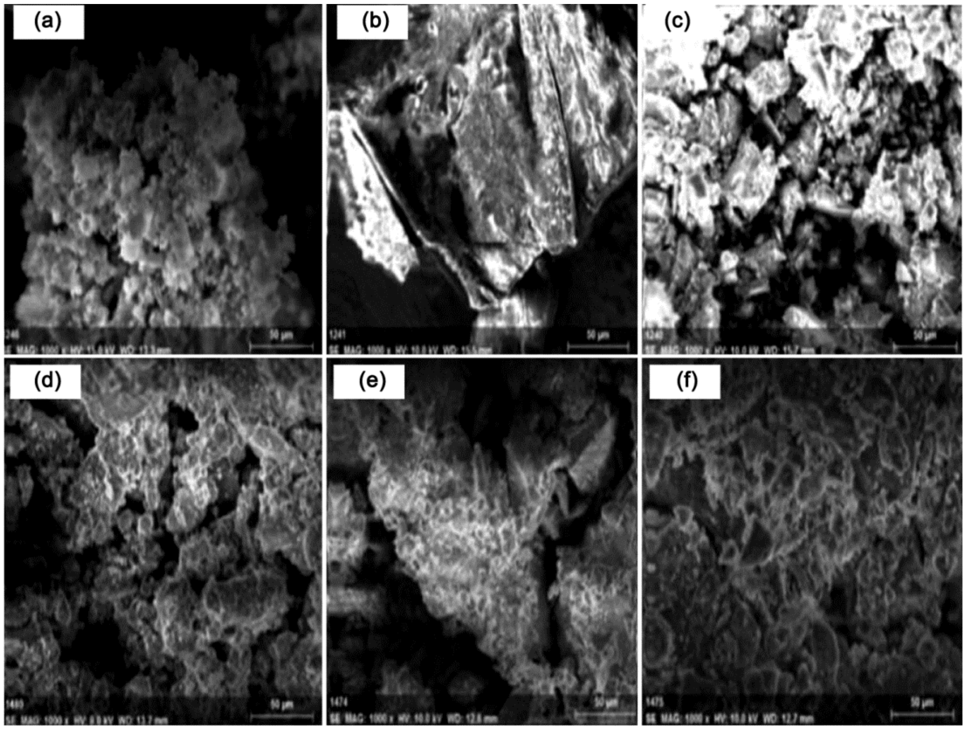


Fig. 3 — The SEM images of: (a) pure silica gel (Sg), (b) pure chitosan (Ch); and for silica-based chitosan biocomposites of: (c) SChC1 (20 mL : 2%), (d) SChC2 (20 mL : 3%), (e) SChC3 (20 mL : 4%), and (f) SChC4 (20 mL : 5%).

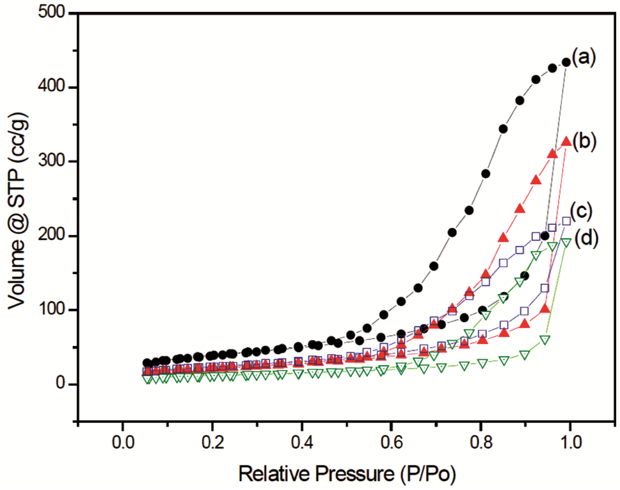


Fig. 4 — The adsorption-desorption isotherm for silica-based chitosan biocomposites of: (a) SChC1 (20 mL : 2%), (b) SChC2 (20 mL : 3%), (c) SChC3 (20 mL : 4%), and (d) SChC4 (20 mL : 5%). The measurements are made at 77 K.

of the chitosan raw material (see data in Table 1). The observations showed that the more the amount of chitosan is added, the smaller the specific surface area, but this pattern does not occur with the addition of 5% chitosan (SChC4). This may be in line with the morphological observations in SChC3 when mixing silica and 4% chitosan is not very homogeneous, so the aggregation occurs as chitosan buildup occurs on a part of the silica surface so that chitosan is bound unevenly to the silica surface and causes the specific surface area is very significantly different from SChC4.

Adsorption capacity of silica-based chitosan biocomposite

The adsorption characteristic of the biocomposite with variation of the chitosan in the material to remove Cd(II) ion is examined. The adsorption profile of the chitosan-based silica biocomposite was recorded from the concentration of Cd^{2+} after loading (C_t) compare to the original 24 ppm Cd^{2+} (C_0) as presented in Fig. 5, and the adsorption capacity of the biocomposite materials are listed in Table 1. The variation in the immobilised chitosan resulted to the variation of the BET values, influenced the active sites of the material, and promote adsorbtion capacity of biocomposite material to a target ion[43,48,49]. The biocomposites are high in the adsorption capacity with time. The adsorption profiles of the biocomposite are almost similar from one to another but different in the adsorption capacity in related to the variation of the immobilised chitosan in the biocomposite. The highest adsorption was obtained in SChC1 with adsorption capacity of 16.16 mg/g Cd^{2+}. High concentration of chitosan in the biocomposite did not improve adsorption ability toward metal ion.

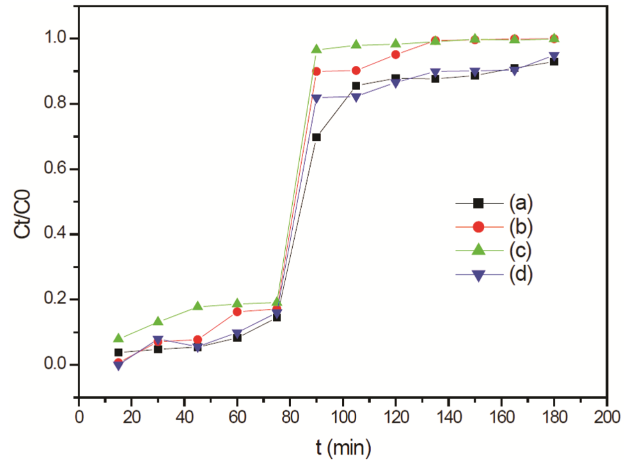


Fig. 5 — The adsorption capacity toward Cd(II) ion by solid-phase extraction method for biocomposite materials of: (a) SChC1 (20 mL : 2%), (b) SChC2 (20 mL : 3%), (c) SChC3 (20 mL : 4%), and (d) SChC4 (20 mL : 5%). The data are recorded from the proportion of the amount of Cd^{2+} after loading (C_t) compared to the original Cd^{2+} (C_0) for 18 minutes.

The capacity adsorption decrease with time which is able to adsorb the ion up to 75 minutes, followed by releasing the ion until obtaining an equilibrium after 120 minutes. The adsorption capacity of the chitosan-based silica biocomposites varies with different concentrations of immobilised chitosan (see results in Table 1). The adsorption capacity is confirmed to be related to the pore size and area where the biggest adsorption capacity was observed in a very small size of the composite particle. The chitosan-based silica biocomposite of SChC1 was the best adsorbent material with having high ability to load metal ion in batch condition.

Conclusion

The silica-based chitosan biocomposite has successfully fabricated through the mixture of precursor Na_2SiO_3 and chitosan solution by using sol-gel method. The interaction between the silica and the chitosan has bind together by the crosslinking agent of glutaraldehyde to form a silica-based chitosan biocomposite. The variation in the concentration of the chitosan that are immobilised into the silica backbone resulted in different properties of the biocomposite material. The biocomposite material prepared from 20 mL silica and 2% chitosan (SChC1) is assigned to be the best silica-based chitosan biocomposite. The biocomposite material SChC1 is amorphous with small crystalline, non-uniform particle, rough surface with having large pore size area between 2θ = 20–24°. The biocomposite has high adsorption capacity towards metals ion which is potential to be applied in the production of low cost adsorbent material.

Acknowledgement

The authors acknowledged the financial support from The Ministry of Research, Technology and Higher Education of the Republic of Indonesia, Directorate Research and Community Service, Directorate General Strengthen Research and Development, Financial Year 2018, under Penelitian Disertasi Doktor, Contract No. 027/UN33.8/LL/2018. The authors also acknowledge Dr. Isli Iriani Pane from the Language Centre of Universitas Negeri Medan who have helped in the English proof reading process.

References

1 Hu Z, Zhang D Y, Lu S T, Li P W & Li S D, *Mar Drugs*, 16 (2018) 273.
2 Marpu S B & Benton E N, *Int J Mol Sci*, 19 (2018) 1795.
3 Rodríguez-Vázquez M, Vega-Ruiz B, Ramos-Zúñiga R, Saldaña-Koppel D A & Quiñones-Olvera L F, *Biomed Res Int*, 15 (2015) 821279.
4 Szymańska E & Winnicka K, *Mar Drugs*, 13 (2015) 1819.
5 Elgadir M A, Uddin M S, Ferdosh S, Adam A, Chowdhury A J K & Sarker M J I, *J Food Drug Anal*, 23 (2015) 619.
6 Kyzas G Z & Bikiaris D N, *Mar Drugs*, 13 (2015) 312.
7 Nurwahyuni I & Sinaga R, *Pak J Bot*, 50 (2018) 667.
8 Nurwahyuni I, *Proceeding of 6thAnnual International Conference on Advances in Biotechnology (BIOTECH 2016) April 2016,* Singapore, (2016) 35.
9 Nurwahyuni I & Sinaga R, *Int J Pharm Bio Sci*, 5 (2014) 863.
10 Wang J, Yang S, Li C, Miao Y, Zhu L, Mao C & Yang M, *ACS Appl Mater Interf*, 9 (2017) 22259.
11 Kumaravel V, Damodaran K, Gandhi S & Krishnan U M, *Bull Mater Sci*, 41 (2018) 133.
12 Simatupang L, Siburian R, Sitanggang P, Doloksaribu M, Situmorang M & Marpaung H, *Rasayan J Chem*, 11 (2018) 819.
13 Yazdani M, Bahrami H & Arami M, *Sci World J*, 13 (2014) 370260.
14 Prabhu S M & Meenakshi S, *Desalin Water Treat*, 53 (2015) 3592.
15 Tamburaci S & Tihminlioglu F, *J Mater Sci Mater Med*, 29 (2018) 1.
16 Maleki A, Haji R F, Ghassemi M & Ghafuri H, *J Chem Sci*, 129 (2017) 457.
17 Venkatesan J, Bhatnagar I & Kim S K, *Mar Drugs*, 12 (2014) 300.
18 Hu J, Liu W, Liu H, Wu L & Zhang H, *Mater*, 11 (2018) 1881.
19 Badwan A A, Rashid I, Al Omari M M H & Darras F H, *Mar Drugs*, 13 (2015) 1519.
20 Saravanakumar A & Dharmendirakumar M, *Indian J Chem Technol*, 25 (2018) 546.
21 Sihombing K, Tamba M C, Marbun W S & Situmorang M, *Indian J Chem*, 57 (2018) 175.

22 Situmorang M & Nurwahyuni I, *Indones J Chem*, 17 (2017) 461.

23 Situmorang M, Gooding J J, Hibbert D B & Barnett D, *Electroanalysis*, 13 (2001) 1469.

24 Situmorang M, Gooding J J, Hibbert D B & Barnett D, *Biosens Bioelectron*, 13 (1998) 953.

25 Teepoo S, Dawan P & Barnthip N, *Biosensors*, 7 (2017) 47.

26 Rao D, Sheng Q & Zheng J, *J Chem Sci*, 128 (2016) 1367.

27 Ang L F, Por L Y & Yam M F, *Plos One*, 8 (2013) 70597.

28 Lee E J, Jun S H, Kim H E, Kim H W, Koh Y H & Jang J H, *J Mater Sci Mater Med*, 21 (2010) 207.

29 Djelad A, Morsli A & Robi M, *Molecules*, 21 (2016) 109.

30 Zhang J, Zhang Y, Li R & Pan Q, *Indian J Chem Technol*, 19 (2012) 161.

31 Gonçalves M C, *Molecules*, 23 (2018) 2021.

32 Baino F, Fiorilli S & Vitale-Brovarone C, *Bioeng*, 4 (2017) 15.

33 Bhullar N, Kumari K & Sud D, *Indian J Chem Technol*, 24 (2017) 560.

34 Budnyak T M, Pylypchuk I V, Tertykh V A, Yanovska E S & Kolodynska D, *Nanoscale Res Lett*, 10 (2015) 87.

35 Li J, Cai C, Li J, Li J, Li J, Sun T, Wang L, Wu H & Yu G, *Molecules*, 23 (2018) 2661.

36 Kong J L, Chang J S & Chang K L B, *J Nanopart Res*, 15 (2013) 1945.

37 Budnyak T M, Yanovska E S, Kichkiruk O Y, Sternik D & Tertykh V A, *Nanoscale Res Lett*, 11 (2016) 492.

38 Gandhi M R & Meenakshi S, *Int J Biol Macromol*, 50 (2012) 650.

39 Shchipunov A Y, Karpenko Y T, Bakunina Y I, Burtseva V Y & Zvyagintseva N T, *J Biochem Biophys Methods*, 58 (2004) 25.

40 da Silva S R, de Albuquerque N J A, de Almeida R M & de Abreu F C, *Materials*, 10 (2017) 1132.

41 Wei P R, Kuthati Y, Kankala R K & Lee C H, *Int J Mol Sci*, 16 (2015) 20943.

42 Zhang B, Hu R, Sun D, Wu T & Yujiang, *Sci Rep*, 8 (2018) 15397.

43 Chernev G, Todorova E, Djambazov S, Salvado I M M & Ivanova J, *J Chem Technol Metall*, 49 (2013) 128.

44 Zhou D, Qi C, Chen Y X, Zhu Y J, Sun T W, Chen F & Zhang C Q, *Int J Nanomed*, 12 (2017) 2673.

45 Nithyaa R, Gomathi T, Sudha P N, Venkatesan J, Anil S & Kim S K, *Int J Biol Macromol*, 87 (2016) 545.

46 Dalagan J Q & Enriquez E P, *Bull Mater Sci*, 37 (2014) 589.

47 Budnyak T, Tertykh V & Yanovska E, *Mater Sci-Medzg*, 20 (2014) 177.

48 Viswanatha N, Pandi K & Meenakshi S, *Int J Biol Macromol*, 70 (2014) 347.

49 Prabhu S M & Meenakshi S, *Desalin Water Treat*, 53 (2015) 3592.