

PAPER • OPEN ACCESS

Preparation of Magnetic Chitosan Beads for Heavy Metal Ions Removal from Water

To cite this article: Rahmi *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **276** 012004

View the [article online](#) for updates and enhancements.

Preparation of Magnetic Chitosan Beads for Heavy Metal Ions Removal from Water

Rahmi*, Fathurrahmi, Lelifajri, Fitri Purnamawati, Rahmawati Sembiring

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Jalan Tgk. Tanoh Abe No. 3 Darussalam, Banda Aceh, Indonesia

*Corresponding author: rahmi@fmipa.unsyiah.ac.id

Abstract. Magnetic chitosan beads have been successfully prepared using Fe_3O_4 and applied for Hg(II) and Cd(II) removal from water. Fe_3O_4 was extracted from Aceh iron sand using co-precipitation method. The preparation of magnetic chitosan beads was conducted with several contents of chitosan and Fe_3O_4 . The obtained magnetic chitosan beads were characterized using XRD, FTIR, and SEM. XRD pattern of magnetic chitosan bead was broader and has a lower intensity than chitosan that confirmed the decrease in chitosan crystallinity. FTIR and SEM data confirmed the formation of magnetic chitosan beads. Adsorption study was performed for Hg(II) and Cd(II) removal from water. The adsorption capacities of magnetic chitosan beads for Hg(II) and Cd(II) were 0.4 and 3.04 mg/g, respectively which were higher than adsorption capacities of pure chitosan.

Keywords: Magnetic chitosan, beads, heavy metal ions, adsorption

1. Introduction

Chitosan is a biopolymer produced from the chitin deacetylation process using alkali. Chitosan is widely used in various fields of industry such as health, cosmetics, agricultural, and livestock industries [1,2]. Chitosan is used as a coagulant in wastewater treatment, moisturizer, seed coating, anti-cancer/anti-tumor, anti-cholesterol, additional animal feed, contact lenses, fat solvent, food preservatives, and adsorbent [3]. As an adsorbent, chitosan obtained much attention due to the nature of chitosan that is not poisonous, biodegradable, and abundantly available [4,5]. However, chitosan in pure form has weaknesses such as high solubility at low pH and limited mechanical properties. Besides, chitosan is usually used as a powder adsorbent. The fine chitosan size makes chitosan very difficult to separate from the solution after the adsorption process [6]. Therefore, efforts should be made to modify chitosan.

Some researchers have reported some modifications of chitosan with the purpose to improve chitosan stability in acidic conditions. Liu *et al.* modified chitosan by converting chitosan into magnetic chitosan [7]. Magnetic chitosan is easily separated from the solution after an adsorption process using external magnet [8,9]. The magnetic chitosan was prepared using commercial Fe_3O_4 . The use of commercial Fe_3O_4 results in expensive adsorbent. Whereas, it is known that iron sand contains Fe_3O_4 that can be used as a magnetic resource. Besides, Indonesia is an archipelago consisting of thousands of islands. Every island is surrounded by beautiful beaches with abundant sand. The sand contains valuable minerals such as iron, titanium, silica, and other elements [10].



Based on the previous studies, the primary magnetic mineral in iron sand was magnetite (Fe_3O_4) [11,12].

Based on the above description, in this work chitosan was modified with Fe_3O_4 extracted from Aceh iron sand. The Fe_3O_4 extraction from iron sand was conducted by a co-precipitation method using HCl and NH_4OH . The magnetic chitosan beads preparation was performed with several ratios of Fe_3O_4 /chitosan. The obtained magnetic chitosan was characterized using SEM, FTIR, and XRD. Its adsorption capacity was examined for adsorption of mercury and cadmium.

2. Methods

2.1. Materials

Iron sand was collected from Aceh. Chitosan (deacetylation degree: 75.0-85.0%) was obtained from Tokyo Chemical Industry Co., Ltd. Japan.

2.2. Fe_3O_4 isolation

Iron sand (15 g) was added to beaker glass containing 100 mL HCl 12 M and stirred at 70 °C for 30 minutes. The solution was then filtered using a filter paper to separate undissolved particles. NH_4OH was dropped into solution while stirred and heated at 70 °C for 30 minutes until a black precipitate was formed [13,14]. The obtained black precipitate (Fe_3O_4) was dried at 70 °C for 2 hours.

2.3. Preparation of magnetic chitosan beads

Chitosan (0.35 g) was dissolved in 20 mL acetic acid (2%) and stirred for 2 hours to form a chitosan solution. Fe_3O_4 particles (0.5 g) were added to chitosan solution and for 2 hours. Dope solution was added to a syringe and dropwise into NaOH solution (3 M). The magnetic chitosan beads formed in the NaOH solution were filtered and washed several times until a neutral pH reached. The magnetic chitosan beads were dried in the oven overnight at a temperature of 40 °C. The same procedure was conducted for several ratios of chitosan/ Fe_3O_4 .

2.4. Adsorption experiments

Magnetic chitosan beads (0.1 g) were added to Erlenmeyer flask which contained 25 mL of the heavy metal ion solution. The initial concentration of the heavy metal ion solution was 25 ppm. The solution was stirred at 150 rpm for 40 minutes. After adsorption, magnetic chitosan beads were removed from solution using a permanent magnet.

2.5. Instrumentation

Heavy metal ion concentrations were determined by using Shimadzu AA-6300 Atomic Absorption Spectrophotometer. FTIR spectra of materials was obtained using Shimadzu FTIR-Prestige 21 Series FTIR Spectrometer, where spectral scanning was conducted from 4500 to 400 cm^{-1} . The XRD patterns were detected utilizing Shimadzu XRD-700 Series X-Ray Diffractometer. It was operated at 40 kV and 30 mA which produced $\text{Cu}_{K\alpha}$ with $\lambda = 0.154$ nm in the range of $2\theta = 10-80^\circ$ using a step size of 0.02 °/min. SEM images were obtained with JSM-6510A/JSM-6510LA (Analytical/Analytical low vacuum SEM).

3. Results and Discussion

3.1. Structural Characteristics

XRD patterns of iron sand and Fe_3O_4 isolated from iron sand are shown in Figure 1. Both XRD patterns show similar peaks that typical for Fe_3O_4 . It was due to the most component of iron sand was Fe_3O_4 . However, the XRD pattern of Fe_3O_4 extracted from iron sand (Figure 1b) shows a broader and lower intensity, which indicated a small crystallite size [15]. XRD pattern of Fe_3O_4 exhibits broad

peaks at 2θ value of 35.98° , 43.72° , 56.68° , and 63.42° which were attributed to the (311), (400), (511) and (440) planes, respectively (JCPDS reference no 00-001-1111) [16].

Figure 2 shows the SEM image of Fe_3O_4 particles which was observed at a magnification of 20,000x. The SEM image exhibits an irregular shape of Fe_3O_4 particles with various particle sizes. It is a good agreement with previous work reported by Daoush related to synthesis of Fe_3O_4 nanoparticles by co-precipitation method [17].

Based on EDS data of Fe_3O_4 (Figure 3), the most elements contained in the sample are Fe and O elements, where Fe element has a mass percentage of 56.59%, and O element has a mass percentage of 34.18%. There are several minor elements contained in the sample such as C, Cl, and Al elements with a mass percentage of 7.39%, 1.21%, 0.62%, respectively. It showed the presence of impurities in the sample, but their contents were meager. Several studies also reported the presence of impurities in extracted Fe_3O_4 [18,19].

Figure 4 shows photo images of magnetic chitosan beads with several Fe_3O_4 /chitosan ratios. The best shape of magnetic chitosan beads was obtained at a ratio of 58.82% (Figure 4f). Figure 4a shows magnetic chitosan beads with a ratio of 83.33%, where they formed an irregular shape. It was due to the high content of Fe_3O_4 particles which made chitosan as a matrix could not bind them well to form bead shape.

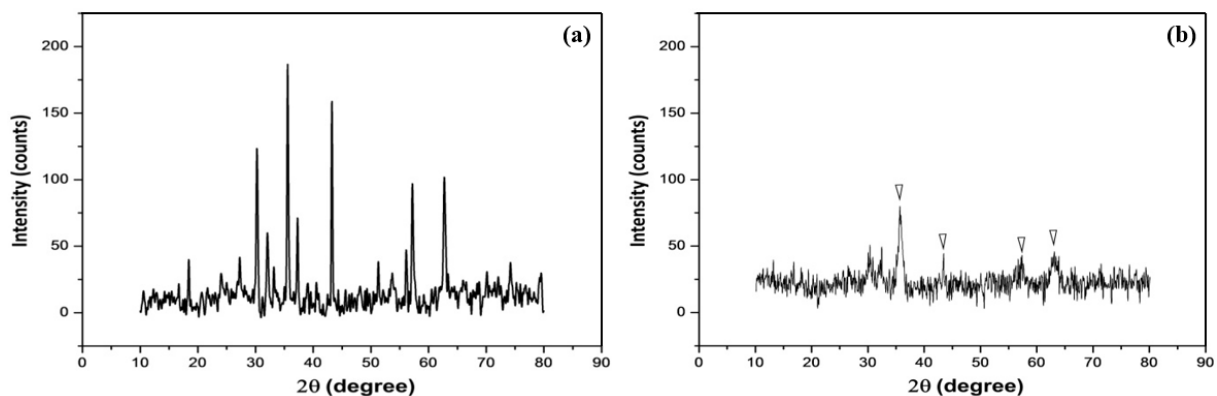


Figure 1. XRD patterns of iron sand (a) and Fe_3O_4 (b)

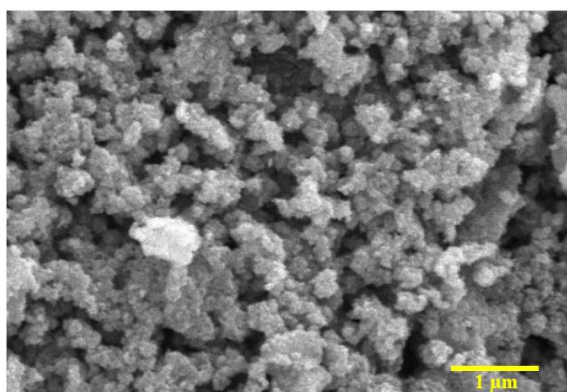


Figure 2. SEM image of Fe_3O_4 particles

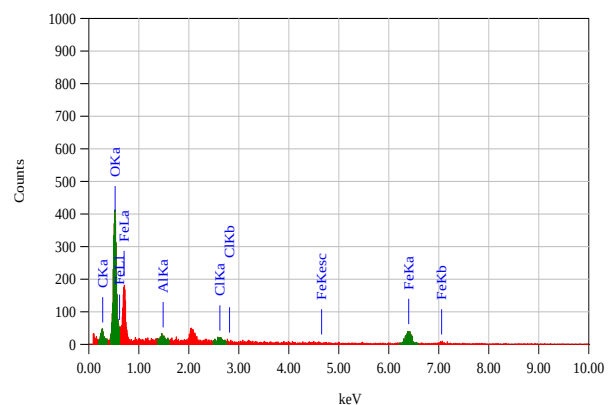


Figure 3. EDS data of Fe_3O_4

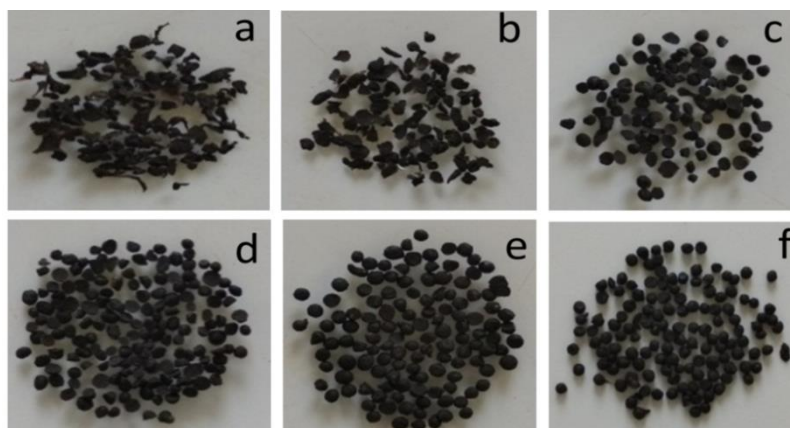


Figure 4. Photo images of magnetic chitosan with several Fe_3O_4 /chitosan ratios of (a) 83.33, (b) 76.92, (c) 71.42, (d) 66.66, (e) 62.50, and (f) 58.82%

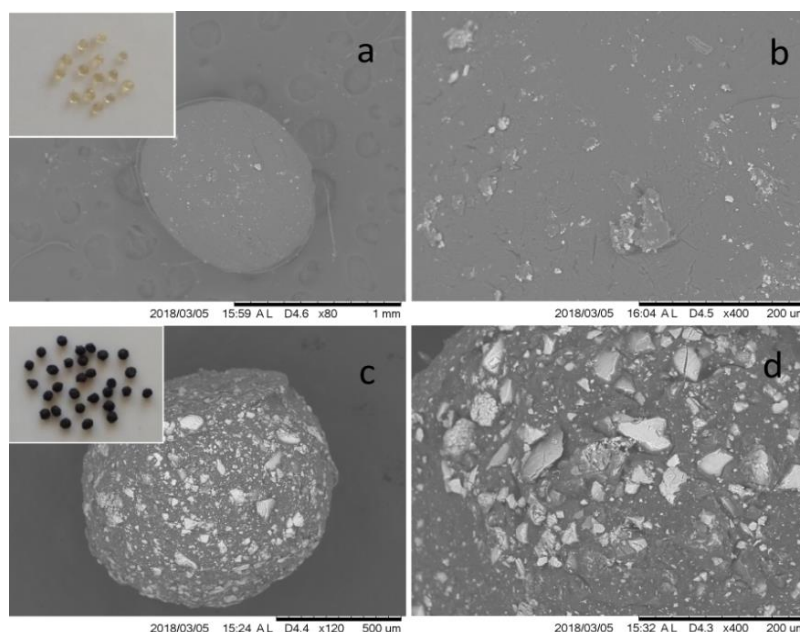


Figure 5. SEM data of (a, b) chitosan beads and (c, d) magnetic chitosan beads

Figure 5 shows SEM images of chitosan beads (a, b) and magnetic chitosan beads (c, d) with different magnifications. At 400x magnification, the surface of chitosan beads was smooth compared to magnetic chitosan beads. It was due to the distribution of Fe_3O_4 particles in magnetic chitosan beads [20], where Fe_3O_4 particles embedded in chitosan beads [16]. Figure 5d shows some Iron oxide (Fe_3O_4) particles were fully coated by chitosan and some others emerged in the surface of the beads. The results confirmed the formation of chitosan beads and magnetic chitosan beads.

FTIR spectra of chitosan beads and magnetic chitosan beads are shown in Figure 6. FTIR spectrum of chitosan beads is shown in Figure 6a. It shows $-\text{NH}_2$ stretching vibration at a wavenumber of 3427.51 cm^{-1} . The band at a wavenumber of 1633.71 cm^{-1} corresponds with amide stretching vibration. These bands show a typical FTIR spectrum of chitosan. Figure 6b exhibits new bands at wavenumber 580.57 cm^{-1} and 428.20 cm^{-1} which correlate with the vibration of tetrahedral Fe-O and octahedral Fe-O [16]. Compared with the FTIR spectrum of chitosan beads, absorption bands of magnetic chitosan beads show some shifts such as at wavenumbers of 2924.09, 1629.85, 1323.17, and 1031.92 cm^{-1} . These results confirmed the interaction between the two components in the sample.

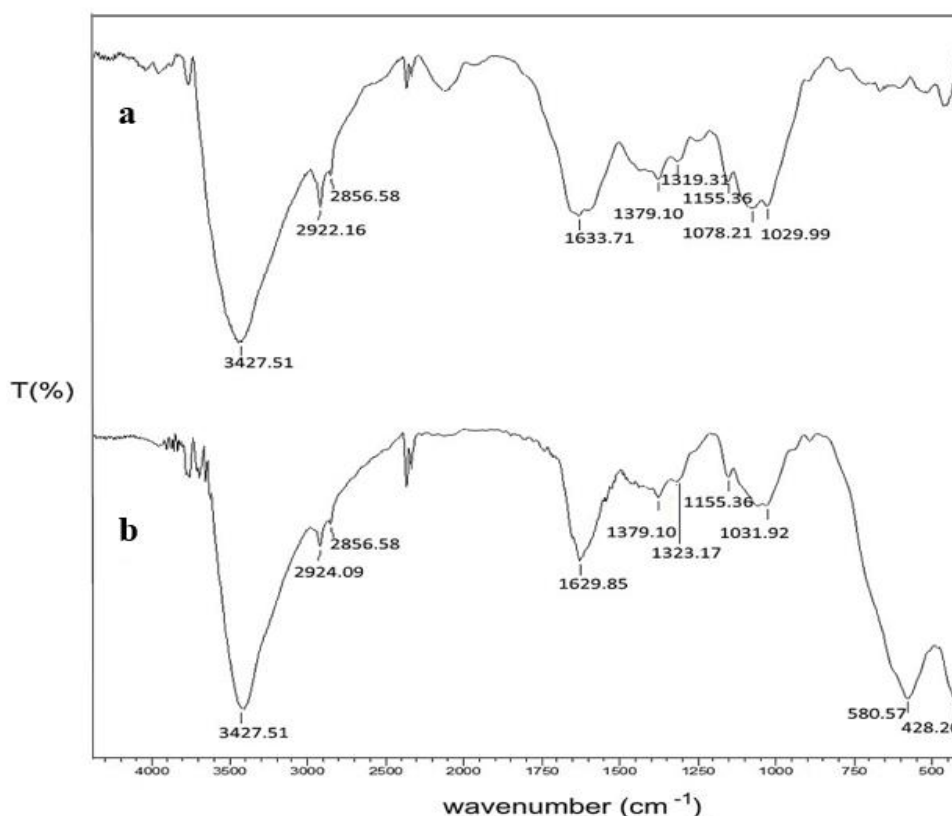


Figure 6. FTIR spectra of (a) chitosan beads and (b) magnetic chitosan beads

Figure 7 shows the XRD patterns of chitosan and magnetic chitosan beads. Figure 7a exhibits $2\theta = 20^\circ$ which is a typical peak for chitosan. After modification with Fe_3O_4 , chitosan lost its crystallinity and generated amorphous materials that was favorable for adsorption process [21]. Typical peaks of Fe_3O_4 were observed in the XRD pattern of magnetic chitosan beads. It confirmed the existence of Fe_3O_4 particles in magnetic chitosan. However, due to their entrapment into chitosan beads, the peaks were suppressed [16].

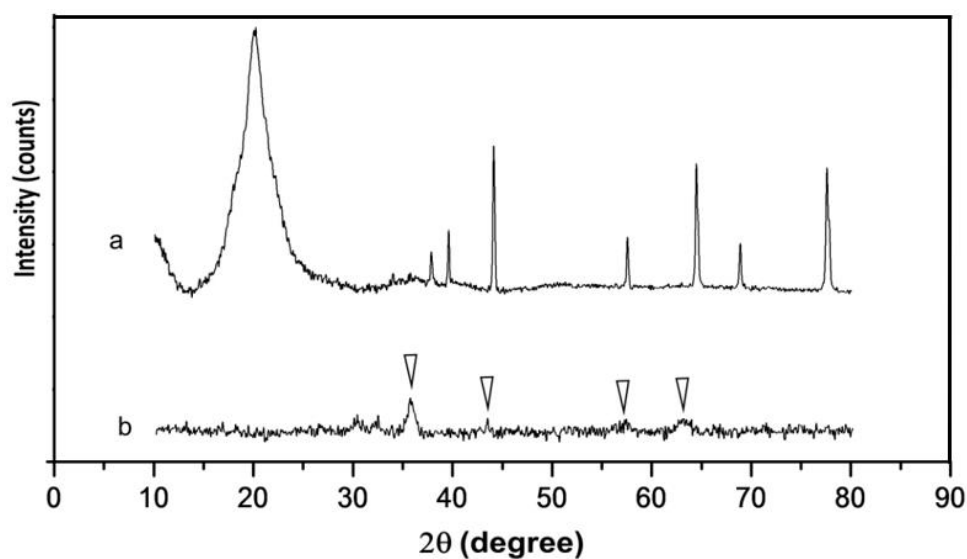


Figure 7. XRD patterns of (a) chitosan and (b) magnetic chitosan beads

3.2. Adsorption studies

The best content of Fe_3O_4 in magnetic chitosan beads as heavy metal ion adsorbent was determined based on the adsorption experiments. The adsorption processes were performed with the same initial concentration and contact time. The results were shown in Figure 8 for mercury adsorption and Figure 9 for cadmium adsorption. The highest adsorption capacity for both Figures was found at Fe_3O_4 content of 58.82%. The adsorption capacity of chitosan beads was lower than the adsorption capacity of magnetic chitosan beads. It was due to Fe_3O_4 particles play an essential role in heavy metal ions removal with specific interactions between heavy metal ions, and Fe formed inner-sphere complexes [22].

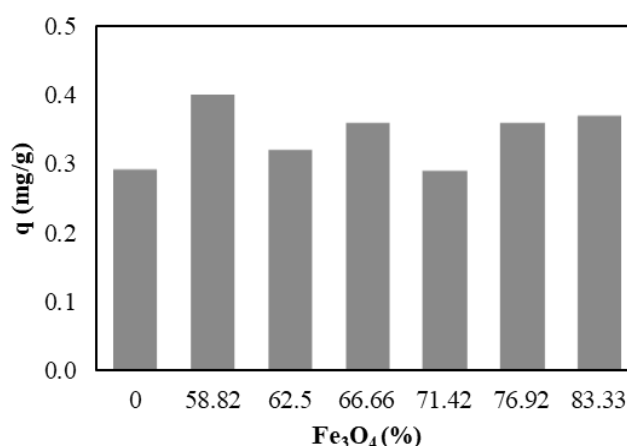


Figure 8. Adsorption capacity (Q) of mercury ions by magnetic chitosan beads with different content of Fe_3O_4

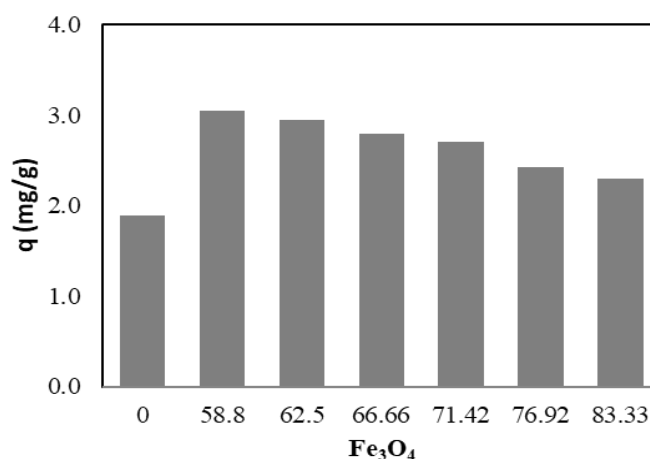


Figure 9. Adsorption capacity (Q) of cadmium ions by magnetic chitosan beads with different content of Fe_3O_4

4. Conclusion

The addition of Fe_3O_4 in chitosan could improve chitosan performance for cadmium and mercury ion adsorption. The best magnetic chitosan beads were found at Fe_3O_4 content of 58.82%. XRD analysis confirmed the decrease in chitosan crystallinity. FTIR and SEM data confirmed the formation of magnetic chitosan beads. The adsorption study was performed for Hg(II) and Cd(II) removal from water. The results showed that magnetic chitosan beads have a higher adsorption capacity than pure chitosan.

Acknowledgements

We gratefully acknowledge the financial support from Direktorat Riset dan Pengabdian Masyarakat, Direktorat Jenderal Penguatan Riset dan Pengembangan Kementerian Riset, Teknologi, dan Pendidikan Tinggi Republik Indonesia (grant number 04/UN11.2/PP/SP3/2018).

References

- [1] Song Z, Li G, Guan F, Liu W 2018 *Polymers*, **10**(389) 1-14
- [2] Senel S, McClure S J 2004 *Advanced drug delivery reviews* **56**, 1467-1480
- [3] Raafat D and Sahl H 2009 *Microbial biotechnology* **2**(2) 186-201
- [4] Wan M, Kan C, Rogel B D, Dalida M L P 2010 *Carbohydrate Polymers* **80**(9) 891-899.
- [5] De Gisi S, Lofrano G, Grassi M, and Notarnicola M 2016 *Sustainable Materials and Technologies* **9** 10-40
- [6] Lv L, Chen N, Feng C, Zhang J, Li M 2017 *RSC Adv.* **7**, 27992-28000
- [7] Liu Z, Wang H, Liu C, Jiang Y, Yu G, Mu X, and Wang X 2012 *ChemCommun.* **48** 7350-7352.
- [8] Paulino A T, Belfiore L A, Kubota L T, Muniz E C, Almeida E B, Tambourgi V C 2011 *Desalination* **275** 187-196
- [9] Fan C, Li K, He Y, Wang Y, Qian X and Jia J 2018 *Science of the Total Environment* **627** 1396-1403
- [10] Ibrahim, Akhyar 2012. *Majalah Ilmiah BISSOTEK.* **7**(1) 44-51.
- [11] Yulianto A, Bijaksana S, Loeksmanto W 2003 *Indonesian Journal of Physics* **14**(2) 63-66
- [12] Tiwow V A, Arsyad M, Palloan P, Rampe M J 2018 *IOP Conf. Series: Journal of Physics: Conf. Series* **997** 012010
- [13] Mufti N, Atma T, Fuad A, Sutadji E 2014 *AIP Conf. Proc.* **1617**, 165-169
- [14] Gunanto Y E, Izaak M P, Jobiliong E, Cahyadi L, Adi WA 2018 *IOP Conf. Series: Journal of Physics: Conf. Series* **1011** 012005
- [15] Yogamalar R, Srinivasan R, Vinu A, Ariga K and Bose A C 2009 *Solid State Communications*, **149** 1919-19
- [16] Malwal D, Gopinath P 2017 *Colloid and Interface Science Communications* **19** 14-19
- [17] Daoush W M 2017 *J Nanomed Res* **5**(3): 00118
- [18] Sukirman E, Sarwanto Y, Insani A, Rina T M, Purwanto A 2018 *IOP Conf. Series: Journal of Physics: Conf. Series* **1091** 012007
- [19] Jalil Z, Rahwanto A, Mustanir, Akhyar, Handoko E 2016 *AIP Conf. Proc.* **1862**, 030023-1-030023-4
- [20] Denkbass E B, Kilicay E, Birlikseven C, Ozturk E 2002 *Reactive & Functional Polymers* **50** 225-232
- [21] Shariful M I, Sepehr T, Mehrali M, Ang B C, Amalina M A 2018 *Journal of Applied Polymer Science* **135**, 45851.
- [22] An B, Liang Q, Zhao D 2011 *Water Res.* **45** 1961-1972.