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The Role of Modification SBA-15 Mesoporous Silica with CPTMS in Cd Adsorptions

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Abstract. Mesoporous silica SBA-15 was synthesized using Pluronic 123 triblock copolymers as surfactant and functionalized with CPTMS to modify its surface. The synthesis of SBA-15 was prepared at optimized concentration of Pluronic 123 surfactant at 60 mM and showed surface area of 831.996 m^2/g determined by BET N_2 adsorption isotherm test at 77 K. The functionalized product, CPTMS-SBA-15 on the other hand has lower surface area at 711.061 m^2/g. This very high surface of CPTMS-SBA-15 and pure SBA-15 were used as adsorbent of Cd from industrial waste water using laboratory water samples. CPTMS-SBA-15 showed lower surface and pore size in comparison with pure SBA-15 but the effectiveness in adsorption of Cd was found higher than pure SBA-15. In this study, we compared the percentage of Cd removal using CPTMS-SBA-15 and pure SBA-15 systems. The materials were characterized by XRD, the presence of organic group was demonstrated by FTIR, and the ions concentration in solution after adsorption process was determined by AAS.

1. Introduction

According to World Bank, the population growth in Indonesia has reached 1.2% per year by 2015, this resulted in rapid development of economic in Indonesia [1]. Therefore, the industrialization process is growing to meet the needs of the community. As the development in industrialization increase, the outcome shows negative effect to environment due to water pollution contains of heavy metals from industrial waste. Unlike any other metals, heavy metals such as Lead, Cadmium, Copper, Zinc, and Chromium has high density than water. These hazardous materials are very dangerous to living things surrounded by them. Especially Cadmium, low exposure to this metal can lead to various symptoms such as vertigo, abdominal pain, vomit, etc. [2]. Thus, remediation of heavy metal ions from industrial water is necessary to prevent further issues.

Nanotechnology has produced a wide range of advanced materials such as mesoporous materials. Mesoporous materials have many wide applications for example as catalysts [3], enzyme carriers [4], and adsorbent material [5]. According to IUPAC, mesoporous materials has pore diameter 2 nm to 50 nm, highly ordered mesoporous structures, and often has large pore volume up to 70% and large surface area (>700 m^2/g) [6], accordingly making it suitable to use in aqueous media as an adsorbent for metals ion adsorption.

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Zhao [7[has developed and synthesized a mesoporous material called SBA-15 (stands for *Santa Barbara Amorphous 15)* in University of California, Santa Barbara. SBA-15 is made of silica and has well-ordered hexagonal mesoporous structure. The average diameter of the pores is 46 to 300 angstroms and the thickness of the silica walls is about 31 to 64 angstroms, therefore it has high mechanical and thermal stability making it a promising material to use in wide applications [7]. SBA-15 was synthesized using triblock copolymer as template because it has gained many interest regarding its simplicity to use in synthesis. In this work, a triblock copolymer surfactant Pluronic P123® ($EO_{20}PO_{70}EO_{20}$, EO = ethylene oxide, PO = propylene oxide) was used as a template because of its ability to form long cylindrical micelles and Tetraethyorthosilicate/TEOS as a silica precursor through sol-gel process. Pure SBA-15 is produced through this process and has surface area up to 746.70 m^2/g [8]. Moreover, large surface area of SBA-15 is preferred in adsorption application.

To increasing its capability as adsorbent materials so that it can interact with metallic cations then SBA-15 was modified or functionalized using functional groups such as $–NH_2$, -SH, -S- etc. Previously, [9] has used multi-amine grafted functional groups contains of amino, di-amino, and tri-amino to modify surface area of pure SBA-15 and obtained a remarkable adsorption capacity of 726 mg Hg^{2+}/g [9]. The SBA-15 capability used as a heavy metal absorber has been demonstrated by [10] on some heavy metals such as zinc (Zn), copper (Cu) and cobalt (Co) using 3-aminopropyl-triethoxysilane (APTES) and salicylaldehyde (SA) as functional group. The functionalized SA-SBA-15 showed a remarkable adsorption capacity for Cu^{2+} compared to other metals [10]. In this present study, we had two goals. Firstly, use (3-Chloropropyltrimethoxysilane) or CPTMS as salinization agent to modify the surface area of pure SBA-15 on Cd adsorption capacity. Other than functional groups mention earlier, CPTMS has Chlor atom to accommodate single electron pair to metallic cation so that it interacts strongly. The process of SBA-15 functionalization with CPTMS has been done by Asgari et. al [5] which is used as a lead metal ion absorbent material. Secondly, we studied the adsorption capacity of functionalized SBA-15 with CPTMS in Cd adsorption application.

2. Experimental

2.1 Materials

Materials were prepared to synthesize silica mesoporous SBA-15 through sol-gel process. Tetraethyorthosilicate/TEOS was purchased from Merck and used as silica precursor, as template Pluronic P123® was purchased from Sigma Aldrich, 2 M HCl, ethanol, and distilled water were used solvent. (3-Chloropropyltrimethoxysilane)/CPTMS and toluene were purchased from Sigma Aldrich and used for functionalization of SBA-15. All of materials were used without further purification.

2.2 Synthesis SBA-15 and functionalization method

SBA-15 material was synthesized using sol-gel process. The sol-gel process was conducted in very acidic condition to allow self-assembly of silica occurs in wet template. Firstly, three solutions were prepared. 5 ml ethanol was mixed with 31.25 gram of TEOS then stirred for 30 min in room temperature. To create acidic condition, second solution was made of 5 ml of ethanol and 10 ml of HCl (2 M). Then, another 10 ml of ethanol was mixed with 50 ml of distilled water and stirred with the second solution for 30 min in room temperature making it third solution. Secondly, the first solution was added to the third solution and stirred for another 30 minutes in room temperature. The mixed solution was refluxed for 2 h at 50-60^oC. The TEOS solution was ready to be use in further step.

The next step was synthesizing Pluronic P123® surfactant template. Pluronic P123® with optimum concentration 60 mM based on Dhaneswara et. al [8] was dissolved in 10 ml HCl (2 M) and 25 ml ethanol. This solution was added dropwise into the previous TEOS solution and then the mixture was stirred until it turned to gel. The resulting gel was dried in furnace for 1 h at 100^oC and then calcined for 5 hours. Mesoporous material SBA-15 was ready for adsorption measurement.

The surface modification of SBA-15 was obtained by following this procedure. First, 0.8 gram of synthesized SBA-15 was suspended in 25 ml of toluene. Second, 5.6 ml of CPTMS was added dropwise to the suspended SBA-15 solution. Then, the mixture was kept under reflux for 24 h at 110^{o}C in a round bottom flask. The obtained precipitate was filtered, washed with toluene and ethanol, and then dried for another 24 h at 100^{o}C. The final product will be referred as CPTMS-SBA-15.

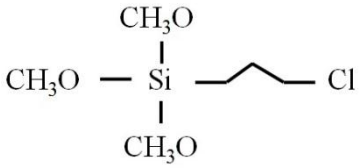

Figure 1. Schematic illustration of chemical structure of SBA-15.

2.3 Cd ion adsorption tests

To determine optimum amount of adsorbent for maximum removal of Cd^{2+} ion therefore initial Cd^{2+} ion concentration of 50 mg/L were prepared with various amount of adsorbent which is 40 mg/L, 80 mg/L, and 120 mg/L were added to 25 ml ion solutions. Hence, adsorption of Cd^{2+} ion with various concentrations were carried out using the determined optimum amount of adsorbent.

99,999% cadmium ions were dissolved in distilled water therefore the cadmium ion solutions with initial concentrations were prepared for adsorption tests. Initial concentration of cadmium ion solutions was 50 mg/L, 100 mg/L, 250 mg/L, 400 mg/L, and 500 mg/L. Optimum amount of adsorbent and 25 ml of cadmium ions solutions were placed in vials and stirred for 15 min The adsorption tests were carried out in room temperature at the rate around 100 rpm. Furthermore, the adsorbents were filtered from the resulting mixtures.

2.4 Characterization

To obtain characteristic of the samples, various characterizations should be done. Crystal structure and orientation of SBA-15 and CPTMS-SBA-15 were measured using small-angle x-ray diffraction. The XRD patterns were carried out within 2θ range from 0^{o} to 10^{o} with step size 0.02^{o} and time 76.8 per step using Cu Kα radiation. Quantachrome adsorption-desorption equipment were used to obtain information about N_2 adsorption-desorption isotherm, mesoporous volume, and pore size of the products and performed at 77 K and specific surface area of the products were calculated using Brunauer-Emmer-Teller (Quantachrome) method. Fourier transform infrared (PerkinElmer) spectra were prepared to determine the functional groups. Transmission electron microscopy (Tecnai G2 spirit Win) were performed to obtain information about the mesostructure of the products. The initial and the remaining metal concentration in solutions were measured via atomic absorption spectrophotometry (Shimadzu).

3. Result and Discussion

3.1 SBA-15 and CPTMS-SBA-15 mesoporous materials comparison

In this paper, mesoporous material SBA-15 has been functionalized successfully with TEOS and Pluronic P123® at concentration 60 mM. As shown in figure 1, Cl lies within the end of the CPTMS functional group. Surface characteristic such as pore diameter, pore volume, and specific surface area of SBA-15 must be analyzed, to get information about the effect of Cl on the surface of SBA-15. The surface observation was conducted using BET. The results for SBA-15 and CPTMS-SBA-15 are shown in table 1.

Table 1. The surface characteristic of SBA-15 and CPTMS-SBA-15 using BET.

	Pore Diameter (Å)	Pore Volume (cc/g)	Specific Surface Area (m^2/g)
SBA-15	29.203	265.161	831.996
CPTMS-SBA-15	28.521	199.649	711.061

3.1.1 Structure characteristic of SBA-15 and CPTMS-SBA-15

Table 1 shows in comparison with surface characteristics of non-functionalized SBA-15, the surface area of CPTMS-SBA-15 is much narrow than pure SBA-15 so do its pore volume and pore diameter. The result shows that pore volume and surface area of CPTMS-SBA-15 were decreased by 25% and 15% compared to non-functionalized SBA-15. It indicated that CPTMS-SBA-15 gas uptake/adsorption capacity is lower than non-functionalized SBA-15. This outcome was obtained by the adsorption-desorption curve exhibits in figure 2.

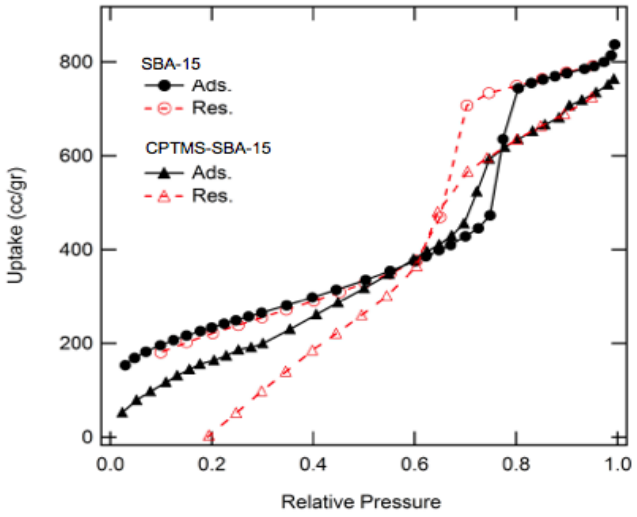

Figure 2. The N_2 adsorption-desorption isotherm curve of non-functionalized SBA-15 and CPTMS-SBA-15. Both curves exhibit type IV with H1 type of hysteresis adsorption isotherm.

Figure 2 reveals that all materials exhibit irreversible type IV adsorption-desorption isotherm with H1 type of hysteresis in relative pressure range from 0.6 to 0.8 for non-functionalized SBA-15 and from 0.6 to 0.73 for CPTMS-SBA-15 because of the high concentration of Pluronic P123®. According to IUPAC classification, type H1 is associated with porous materials consisting of well-ordered cylindrical-like pore channels [11]. As previously reported by (Dhaneswara et. Al, 2016), large pore size indicates more homogenous pore structure. Accordingly, to small surface area and pore volume of CPTMS-SBA-15, instead of having more homogenous pore, CPTMS-SBA-15 has more heterogeneity pore structure than non-functionalized SBA-15. It can be seen from both curves that before and after the functionalization, the curve shows stable shape indicating there was no pore structural changes occurred and the uniform mesoporous structure existing was still in its original state.

According to BET method, the following results of CPTMS-SBA-15 which is pore diameter, pore volume, and specific surface area has smaller value than non-functionalized ones. However, it indicates that the adsorbent surface was under modification. The reduction of this factors occurred

because of the functionalization agent of CPTMS was found inside the pores too. Pore size distribution curves for CPTMS-SBA-15 and SBA-15 are shown in Figure 3 shows that SBA-15 has narrow pore size distribution with maximum pore diameter around 29.203 Å. On the other hand, the pore size of CPTMS-SBA-15 is decreased even though the distribution was nearly the same. Furthermore, the peak of CPTMS-SBA-15 in the curves is lower in comparison with non-functionalized SBA-15. It is indicating that CPTMS-SBA-15 has less order structure. This result has previously reported by Chong et. Al [12].

Figure 4 shows FTIR result for SBA-15 and CPTMS-SBA-15. The FTIR spectrum of SBA-15 and CPTMS-SBA-15 shows typical bands at 2950-2850 cm^{-1}, this belong to symmetric-asymmetric stretching of the C-H bonds. A band at 722 cm^{-1} was corresponded to vibration of Si-C bonds. A band at about 500 cm^{-1} was also identified as C-Cl stretching vibration. These results confirm the successful functionalization of SBA-15. Therefore, we can imply the CPTMS-SBA-15 structure form these result (shown in figure 7).

In figure 5, SAXS patterns of both materials SBA-15 and CPTMS-SBA-15 were shown. The XRD patterns clearly display broad peak of 2 θ at around 0.3683 degree and another peak at around 0.6138 for both materials. The SAXS patterns clearly display three peaks, first peak (100) is corresponding to surface walls. The other two peaks (110) and (200) show the hexagonal structures from SBA-15 materials. After functionalization, the height of the peak was reduced due to the presents of Cl and the possibility of the structure alteration.

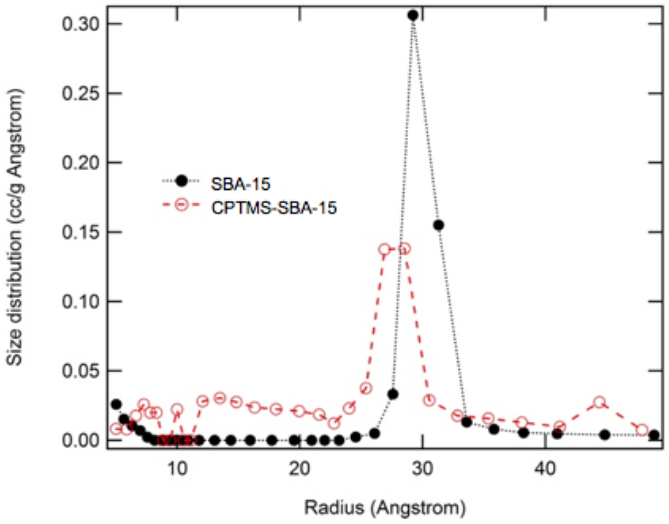

Figure 3. BET method for pore size distribution of SBA-15 and CPTMS-SBA-15. The pore size of CPTMS-SBA-15 is narrower compared to SBA-15 even though the distribution was nearly the same.

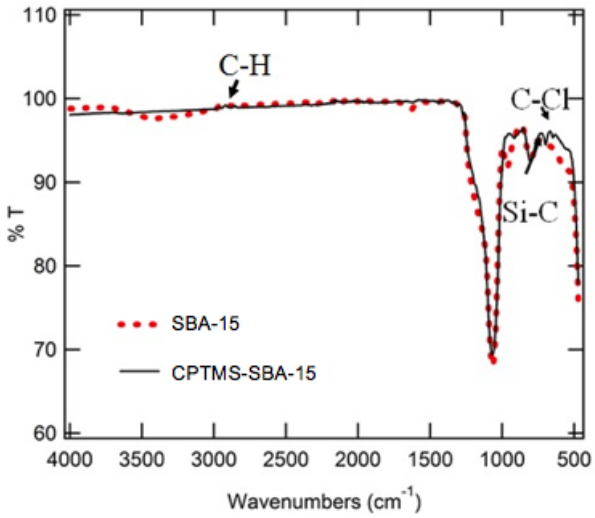

Figure 4. FTIR spectra for SBA-15 and CPTMS-SBA-15

3.1.2 Morphology of SBA-15 and CPTMS-SBA-15

In figure 6, figure 6(a) shows a TEM image of SBA-15 while figure 6(b) shows a TEM image of CPTMS-SBA-15. It seen in the figure that CPTMS-SBA-15 has vivid surface compared to SBA-15 due to modification process with Chlor and methyl. From both figures, we can see that both materials have nano-sized pore.

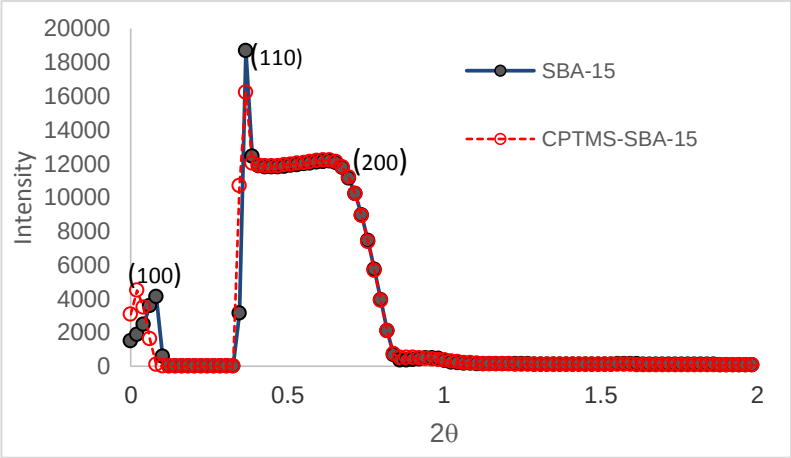

Figure 5. SAXS patterns of SBA-15 and CPTMS-SBA-15.

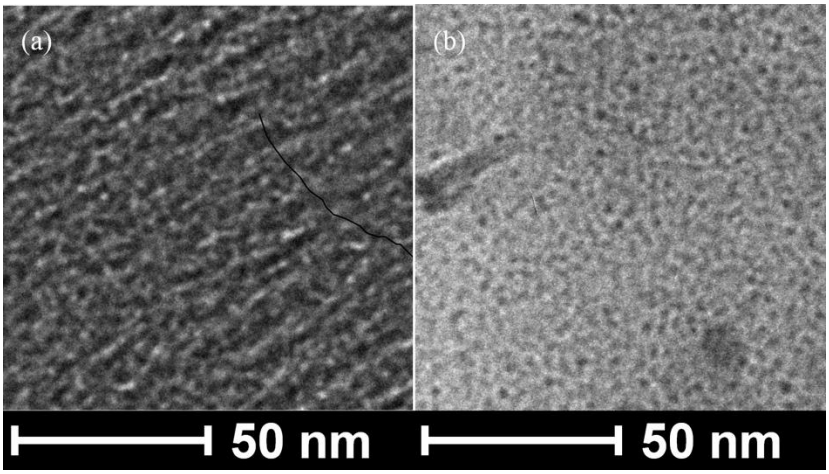

Figure 6. The TEM image of (a) SBA-15 and (b) CPTMS-SBA-15

3.2 Cd ion adsorption studies

Table 2 shows the percentage of removal for both adsorbent materials and the results show that Cd^{2+} ion removal for CPTMS-SBA-15 is higher in comparison with non-functionalized SBA-15. Result shown in Figure 8, it is observed that increasing the adsorbent amount will increase the percentage of removal and finally the maximum extraction of cadmium ions was achieved using 120 mg/L of CPTMS-SBA-15 with percentage of removal reaches 63.98%. Hence, 120 mg/L of CPTMS-SBA-15 were used in order to determine removal efficiency of Cd^{2+} ion.

In figure 8, as can be seen that CPTMS-SBA-15 has higher removal percentage in adsorbing heavy metal which is cadmium regarding this work compared to non-functionalized SBA-15, even though the surface area of CPTMS-SBA-15 is lower than non-functionalized SBA-15. As expected, functionalization in SBA-15 surface affects reduction in pore size and pore volume as obtained using BET method because of BET surface and volume are standardized towards pure silica weights as shown by Mureseanu et al. [10] . This is confirming the role played by organic functional groups from CPTMS were located both in the surface and inside the mesoporous pores. As result in reducing the BET surface area during modification. However, it does not affect the effectiveness in heavy metal adsorption as investigated in this work. The modification of SBA-15 generates O-Si-Cl bridge as shown in figure 7. Furthermore, this bridge may take Cd better than the surface with only Si-O.

The Cd^{2+} ion adsorption tests were carried out to determine removal efficiency of the adsorbent toward Cd^{2+} ion. The quantity of Cd removal was investigated by measuring the initial and final concentration of Cd^{2+} ion. In figure 9, the effect of initial concentration of Cd^{2+} ion shows that 120 mg/L of adsorbent has highest Cd^{2+} ion removal percentage with 50 mg/L Cd^2 ion concentration. This result is in a good agreement with Asgari et al. [5] which is the adsorption process will increase as the increasing of metal ion concentrations if there are unoccupied sites. However, if all the sites are occupied, the amount of metal ion on adsorbent does not increase although the ion concentration in solutions increases.

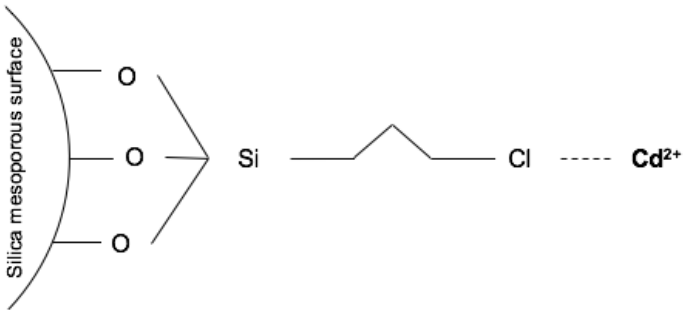

Figure 7. Schematic structure of CPTMS-SBA-15.

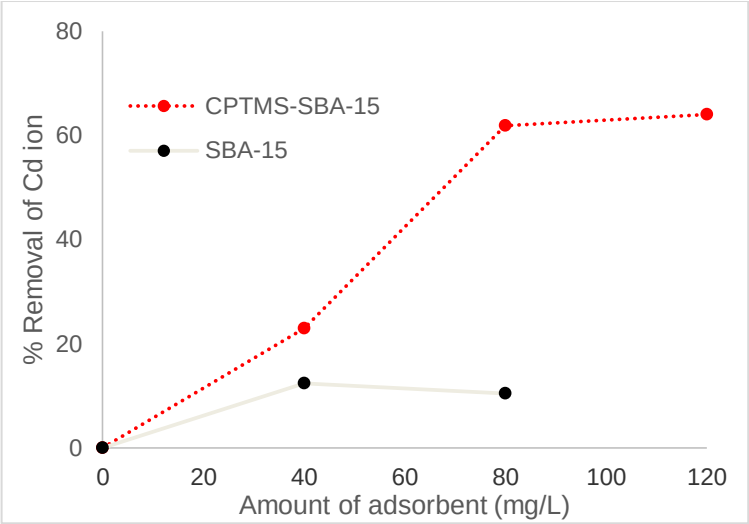

Figure 8. Effect of amount of adsorbent on the removal of Cd ions for SBA-15 and CPTMS-SBA-15.

Table 2. Cd removal of SBA-15 and CPTMS-SBA-15

Adsorbent	Initial concentration (mg/L)	Cd removal	
		Final concentration (mg/L)	Percentage (%)
SBA-15	40	12.39	9.8
	80	10.46	23.8
CPTMS-SBA-15	40	10.59	23
	80	5.24	61.8
	120	4.96	63.9

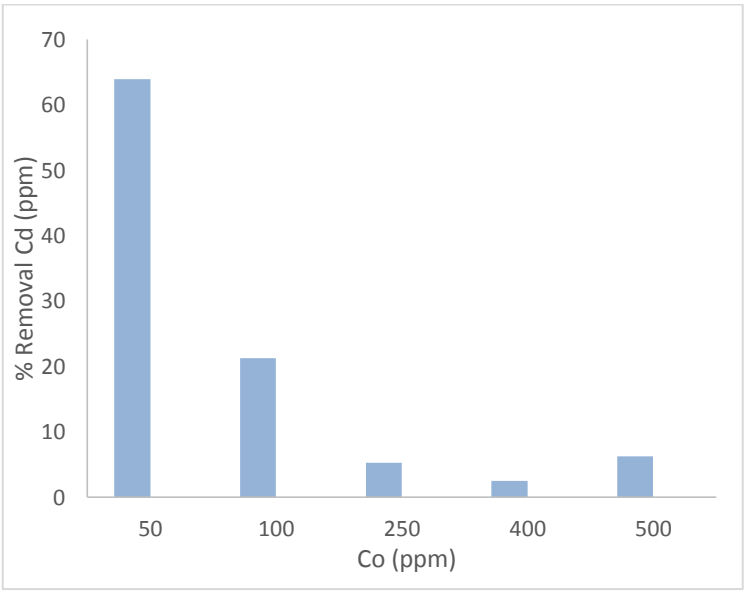

Figure 9. Effect of initial concentration on the removal of Cd^{2+} ions by CPTMS-SBA-15.

4. Conclusion

In this study, SBA-15 was successfully synthesized and functionalized with CPTMS. The functional groups grafted on the SBA-15 surface and inside the pore resulted in smaller surface area, pore size, and pore volume of CPTMS-SBA-15. However, it does not reduce its remarkable adsorption efficiency for heavy metal adsorption. The application of remediation of heavy metals from real samples were demonstrated using laboratory wastewater samples. The functionalized SBA-15 shows higher effectivity for adsorbing Cd^{2+} ion in comparison with non-functionalized SBA-15 using 120 mg/L of adsorbent. Regarding removal effectivity in the effect of initial concentrations of Cd^{2+} ion, 120 mg/L of CPTMS-SBA-15 has highest removal percentage for 50 mg/L initial concentrations.

Acknowledgments

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References

[1] Statistics Indonesia (BPS) 2008 Indonesia Population Projection 2010-2035.
[2] Baselt, R. C., & Cravey, R. H 1995 Disposition of Toxic Drugs and Chemicals in Man. In *Year Book Medical Publishers* (4th ed., Vol. 4th, pp. 105–107). Chicago: Year Book Medical Publishers.
[3] Hung, B.-Y., Kuthati, Y., Kankala, R., Kankala, S., Deng, J.-P., Liu, C.-L., & Lee, C.-H. 2015 *Nanomaterials* ***5***(4) 2169–2191.
[4] Thielemann, J. P., Girgsdies, F., Schlögl, R., & Hess, C. 2011 *Beilstein Journal of Nanotechnology* ***2*** 110–118.
[5] Asgari, M. S., Zonouzi, A., Rahimi, R., & Rabbani, M. 2015 *Oriental Journal of Chemistry*, ***31***(3) 1537–1544.
[6] Cao, G., & Wang, Y. 2004 Nanostructures and nanomaterials: synthesis, properties, and applications
[7] Zhao, D. 1998 *Science* ***279***(5350) 548–552.
[8] Dhaneswara, D., & Sofyan, N. 2016 *International Journal of Technology*, ***7***(6), 1009–1015

[9] Zhang, L., Yu, C., Zhao, W., Hua, Z., Chen, H., Li, L., & Shi, J. 2007 *Journal of Non-Crystalline Solids* ***353***(44–46) 4055–4061.
[10] Mureseanu, M., Reiss, A., Stefanescu, I., David, E., Parvulescu, V., Renard, G., & Hulea, V. 2008 *Chemosphere* ***73***(9) 1499–1504.
[11] Thommes, M. 2004 *Nanoporous Materials - Science and Engineering* (p. 336). London: Imperial College Press.
[12] Chong, M., S., A., & Zhao, X. S. 2003 *The Journal of Physical Chemistry B* ***107*** 12650–12657.