

Selective Adsorption of CPTMS-SBA-15 towards Zinc and Cadmium for Liquid Waste Remediation

Donanta Dhaneswara^{1}, Dewantoro Adhy Putranto¹, Muhammad Bachtiar¹, Jaka Fajar Fatriansyah¹*

¹Departement of Metallurgical and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Kampus Baru UI 16424 Depok, Jawa Barat, Indonesia

Abstract. Mesoporous silica SBA-15 has been synthesized using Tetraorthosilicate as precursor and Pluronic 123 triblock copolymers as template through the sol gel method. The surface of SBA-15 was modified using functionalization agent CPTMS (3-chloropropyl(trimethoxy)silane). SBA-15 was found to have surface area of 831.996 m²/g higher than CPTMS-SBA-15 which has surface area at 711.061 m²/g. Laboratory water samples of Zn and Cd were adsorbed by CPTMS-SBA-15 and SBA-15. The comparison of SBA-15 and CPTMS-SBA-15 indicated that CPTMS-SBA-15 has lower surface and pore size. CPTMS-SBA-15 also has lower effectiveness in adsorption than SBA-15. The comparison between Zn and Cd percentage removal has been studied in this paper. XRD was used for identify the materials. FTIR was used to study the organic group of both SBA-15. AAS was used for determine the adsorption capability of SBA-15.

1 Introduction

The industrialization process in Indonesia has side effects of environmental contamination such as soil, water and air pollution. Soil pollution by heavy metal such as zinc, lead, copper and others in industrial areas in Jabodetabek (Jakarta, Bogor, Depok, Tangerang and Bekasi) is very high and has a bad impact for people around the industrial areas[1]. The population of Indonesia concentrated in the industrial and surrounding areas reaching 6% of Indonesia's population[2], the impact of heavy metal pollution will be enormous. Hazardous heavy metals includes Zinc (Zn), Mercury (Hg), Cadmium (Cd), Chromium (Cr) and others. This waste is discharged and this liquid waste usually flows into rivers around industrial areas for example in Jakarta. Along with the development of the city, it will continuously supply the heavy waste into the river. And it is proven that the rivers located in Jakarta have been contaminated by various types of heavy metals and it is dangerous for local people[3].

Development in nanotechnology has produced many advanced materials and it has benefits more than conventional materials. These materials have an extraordinary properties

* Corresponding author: farhan.delayori@ui.ac.id

compared to conventional materials. One of these materials is the mesoporous silica SBA-15 which has a surface area up to $400\text{m}^2/\text{g}$ [4] which has wide application such as in separation[5,6], optics[7,8], catalyst[9,10] and as nano template materials[11,12]. SBA-15 is a mesoporous silica material which has a uniform hexagonal pore structure. The pore diameter of SBA-15 is between 5 to 15 nm[13] and the thickness of structural walls is 3.1 to 6.4 nm. Based on the SBA-15 large surface area, SBA-15 material is applicable as an adsorbent.

The ability of SBA-15 for heavy metal as an adsorbent has been demonstrated by Mihaela et al.(1998) on some heavy metals such as Zinc (Zn) and Cobalt (Co). SBA-15 that is used for this study is synthesized using Zhang et al.[14] method. This method employs amphiphilic triblock co-polymers. Donanta D. Et. Al [15] has been successfully synthesized SBA-15 using Pluronic 123 with a simpler method. In this study, the SBA-15 will be used as an adsorbent material for Zinc and Cadmium heavy metal. It is expected that our materials can reduce the concentration of Zinc and Cadmium in waste water.

Here, SBA-15 as a mesoporous material is functionalized. Functionalization is purposed to enhance adsorption capability of SBA-15 towards heavy metals. Several agents which have been used for functionalization are CPTMS[16], THPP [16] and APTES[17]. CPTMS has Chlor atom which accommodates single electron pair to metallic cation and it interacts strongly each other. Hence, the present study is aimed to synthesize CPMTS-SBA-15 using the process that has been done by Asgari et al.[16]. The first part of this work discusses the synthesis and characterization of CPTMS-SBA-15 and the last part discusses investigation of the adsorption ability of CPMTS-SBA-15 in zinc(II) and Cd(II) ions removal from aqueous solution.

2 Experimental

2.1 Material

Tetraethoxyorthosilicate (TEOS) which is used as silica precursor was purchased from Merck and Pluronic P123[®] as template was purchased from Sigma Aldrich. 3-chloropropyltrimethoxysilane (CPTMS) and toluene were purchased from Sigma Aldrich. Those materials were used without any purification.

2.2 Synthesis SBA-15 and CPTMS-SBA-15

Sol-gel process was used to synthesize SBA-15 using TEOS as a precursor and surfactant Pluronic 123[®] as a template. There are 4 require basic solution to synthesis of SBA-15. Solution I consists of TEOS with 5 ml ethanol. Solution II was needed to create acidic condition which consists of 10 ml of HCl (2M) with 5 ml ethanol. Solution III consists 50 ml H₂O with 10 ml ethanol and solution IV consists surfactant Pluronic 123[®] with 25 ml of ethanol and 10 ml of HCl (2M). First, solution II and III are mixed. Then, the mixture was further mixed again with solution I by stirring for 30 minutes. The resulting mixture of those three solutions was refluxed at 50°-60°C for 2 hours and then was added drop wisely with solution IV. Then, the solution was dried at 100°C for 1 hours and then calcined at 400°C for 5 hours. Mesoporous SBA-15 material was obtained and ready to use.

Mesoporous SBA-15 was functionalized with (3-chloropropyltrimethoxysilane)/CPTMS. The functionalization process begins by dissolving 0.4 grams of SBA-15 into 25 ml toluene. Then, CPTMS was added dropwise by 2.8 ml into the toluene solution. This solution is refluxed at 110°C for 24 hours. The precipitate of the reflux is filtered and washed using toluene and ethanol. Then, it was dried using an oven at 100°C for 24 hours. The result of this process is called CPTMS-SBA-15.

2.3 Characterization

Both of SBA-15 and CPTMS-SBA-15 were done with various characterizations to obtain their characteristics. Transmission electron microscopy/TEM (Tecnai G2 spirit Win) was used to identify the mesostructure. A PerkinElmer Fourier transform infrared (FTIR) was performed to get the information of functional groups. Small-angle x-ray diffraction (SA-XRD) with Cu K α radiation were used to measure crystal structure and orientation of pure SBA-15 and CPTMS-SBA-15. Nitrogen adsorption-desorption analysis was performed by quantachrome adsorption-desorption equipment at 77K to get the information of mesopores volume, pore size and specific surface area. Determination of zinc and cadmium concentration was conducted using atomic absorption spectrophotometry (Shimadzu).

2.4 Zn and Cd ion adsorption test

To determine the optimum values of SBA-15 as adsorbant of Zn, following procedure is conducted. Initial concentration of 100 mg/L Zn was obtained by dissolving Zn(NO $_3$) $_2$ into distilled water with the variations of adsorbant 100 mg/L, 500mg/L, 1g/L and 1,5 g/L. Solution was stirred for 100 minutes at 300 rpm. Furthermore, this obtained optimum value of adsorbantis used in adsorption experiment of varying Zn concentration of 20 mg/L, 60 mg/L, 100 mg/L and 140 mg/L. Then, the solution was stirred for 100 minutes at 300 rpm. Similar procedure was conducted for Cd adsorption. In this case, 40 mg/L, 80 mg/L and 120 mg/L of adsorbant concentration were used. In Cd adsorption experiment, 50 mg/L, 100 mg/L, 250 mg/L, 400 mg/L and 500 mg/L of concentration were used. The solution was stirred for 15 mins in room temperature at 100 rpm.

3 Result and discussion

3.1 Characterization

Silica mesoporous SBA-15 material has been successfully synthesized with precursor TEOS and surfactant Pluronic P123[®]. CPTMS has been successfully used for functionalization agent for SBA-15. Chlorine as main functional group of CPTMS as shown in the figure1 may increase the adsorption capacity of SBA-15 of heavy metal by trapping cations via ionic interaction. The possibly structure of CPTMS-SBA-15 shown in figure 2 with attached chlor in the end of SBA-15 bond.

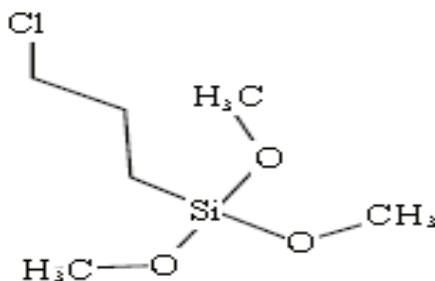


Fig.1. Structure of CPTMS

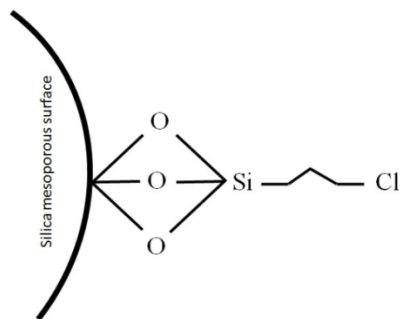


Fig. 2. The Possible Structure of CPTMS-SBA-15

TEM image of mesoporous SBA-15 and CPTMS-SBA-15 can be seen in the figure 3 (a) and 3 (b). The nano sized pores were observed which shows parallel cylindrical pores of 2D hexagonal unit cell as a trademark of SBA-15[18]. Figure 3 (b) shows that the surface of CPTMS-SBA-15 looks brighter which is caused by the modification by methyl and chlor. CPTMS as functionalization agent is found to be dispersed around the SBA-15 as seen as white particles shown in TEM result.

The Small Angle X-Ray Diffraction was used to determine SBA-15 and CPTMS-SBA-15 crystallinity. The samples peak point of SAXRD of 2θ at near 0.3683 and another peak point near 0.6547. Based on figure 4, both of samples show relatively close peak on (100) that clarifies surface walls and peaks of (110) and (200) that clarify pore structure. These three peaks show the samples has 2D hexagonal pore structure [19]. CPTMS-SBA-15 has lower peaks than SBA-15. This is caused by alteration of ordered mesostructure SBA-15 as a result of functionalization of Cl in the surface of mesoporous silica[16].

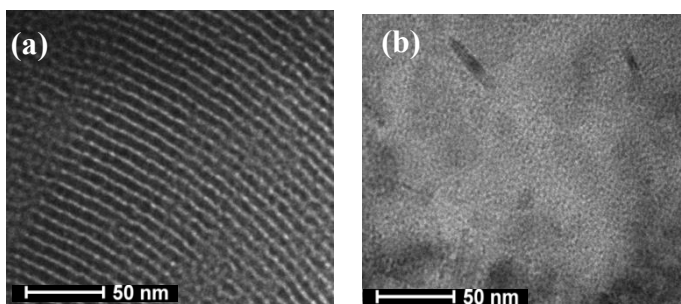


Fig. 3. TEM images for (a) SBA-15 and (b) CPTMS-SBA-15

Fig. 5 shows about the N_2 adsorption-desorption isotherms result of both SBA-15. Both samples show same curves that can be classified as a irreversible adsorption-desorption type IV. Type IV shows possibility of interconnected networks, cyllydrically structure of pores and capillary condensation phenomenon [15]. Hysteresis loop occurs at range 0.6-0.8 elative pressure for SBA-15 and 0.6-0.7 for CPTMS-SBA-15. The hysteresis form is classified as category H1 which is associated with a porous materials containing cylindrical pore channels [15]. From the curves, it shows relatively unchanged form which means that the functionalization did not change the surface/pore structures.

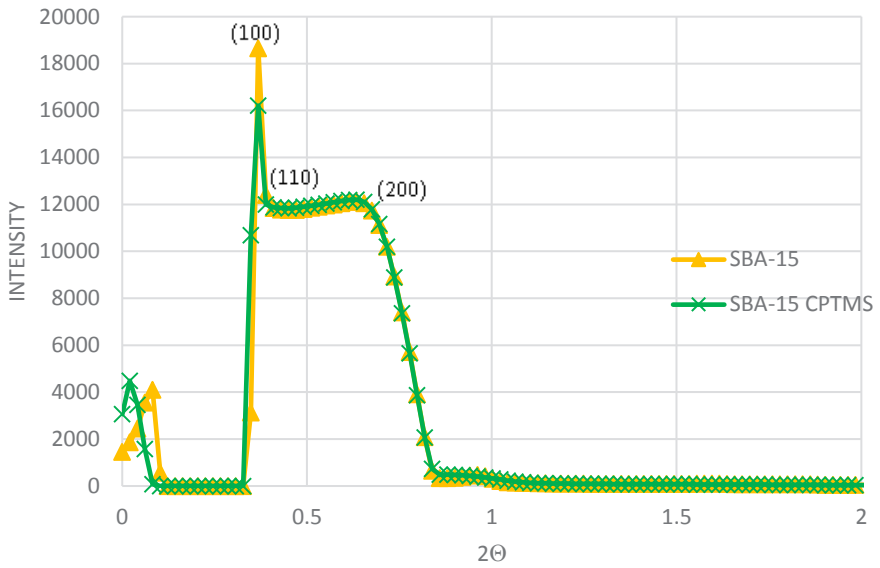


Fig. 4. SAXRD SBA-15 and CPTMS-SBA-15

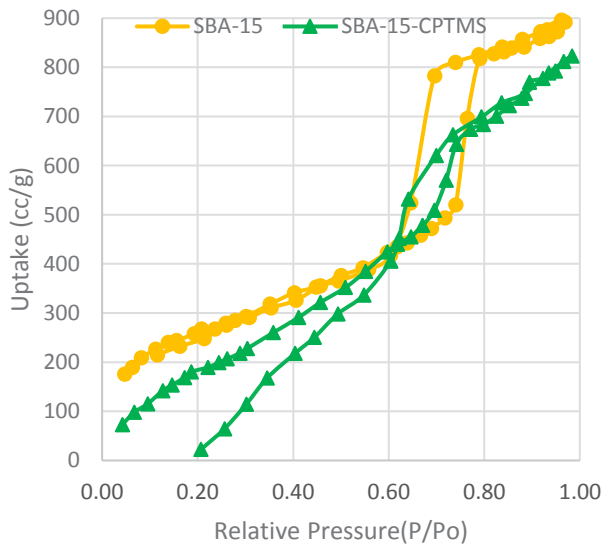


Fig. 5. The N₂ adsorption-desorption curves of SBA-15 and CTPMS-SBA-15

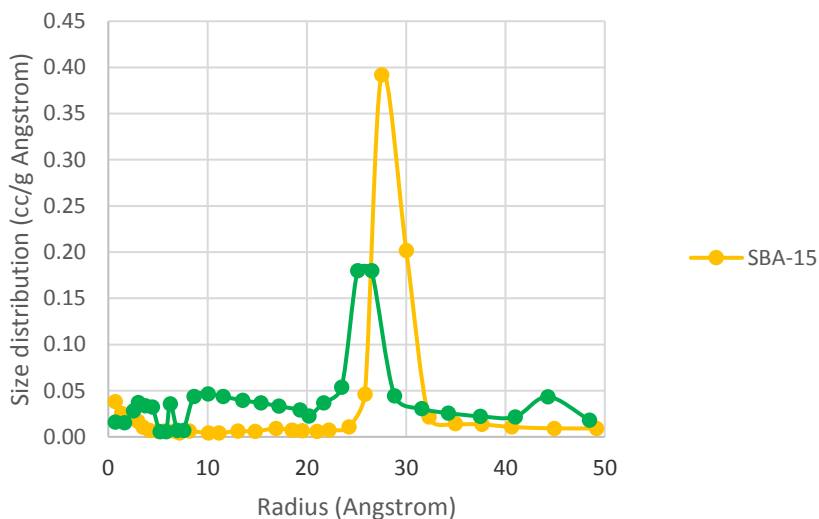


Fig. 6. The size distribution of SBA-15 and CPTMS-SBA-15

Figure 6 shows that the maximum pore diameter with high size distribution curve of SBA-15 is around 29.203Å. CPTMS-SBA-15 has lower pore size with relatively same distribution curve. Functionalized SBA-15 has less ordered structure than pure SBA-15 because the peak of distribution curve is lower. However, it is safe to assume that there is no significant change of pore diameter and structure due to the functionalization.

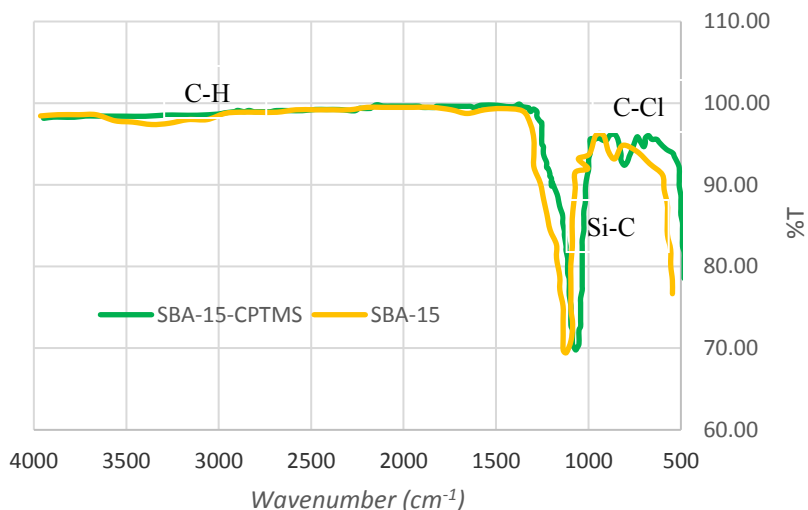


Fig. 7. SBA-15 and CPTMS-SBA-15 FTIR Results

Figure 7 shown that there is symmetric-assymeric stretching of C-H bonds at 2950-2850 cm^{-1} . There is also a vibration of Si-C bond at 722 cm^{-1} . Chlor as a part of functionalization agent has been indentified at 500 cm^{-1} as a C-Cl bond. This means that CPTMS is successfully functionalized onto SBA-15.

The result of BET measurement can be seen in table 1 that shows the diameter of CPTMS-SBA-15 is smaller than SBA-15. Smaller diameter of pore in CPTMS-SBA-15 yields lower specific surface area and pore volume. The lower size of pore, volume and

surface area of CPTMS-SBA-15 infers that the Chlor can be located not only in the surface but also inside the pores. This result is relevant to N₂ adsorption-desorption result in figure 5 which demonstrates that the gas uptake of CPTMS-SBA-15 is lower than SBA-15. The bond between SBA-15 and Chlor also can be identified by observing the decrease of pore diameter of CPTMS-SBA-15.

Table 1. BET result of characteristics of adsorbant

	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

3.2 Adsorbant optimum value

Figure 8 shows about the result of adsorption by varying adsorbant concentration for Zn removal and figure 9 for Cd removal. 0.5 g/L of SBA-15 can remove 66.7% Zn from solution. The highest removal was found for 1.5 g/L of adsorbant which removes 77% of Zn. It can be determined that the optimum concentration of SBA-15 as an adsorbant for Zn removal is 1g/L due to the small disparity between the removal of 1 g/L and 1.5 g/L. This concentration of 1g/L SBA-15 will be used in the next adsorption test of Zn heavy metal.

Figure 9 shows the removal percentage with various SBA-15 and CPTMS-SBA-15 concentration for Cadmium adsorption. The removal percentage of SBA-15 is lower than CPTMS-SBA-15. It shows that the increase of adsorbant concentration increases the removal percentage.

The highest removal was found for the concentration of 120 mg/L which has percentage of removal of 63.98%. This concentration of adsorbant will be used for SBA-15 and CPTMS-SBA-15 in the next adsorption test of Cadmium.

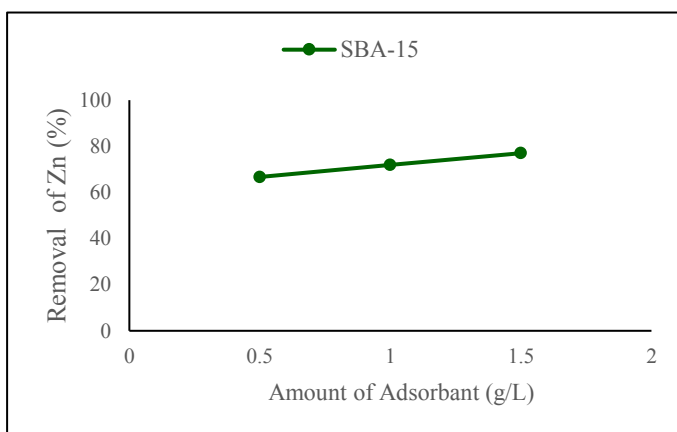


Fig. 8. Effect of amount of adsorbant on Zinc removal

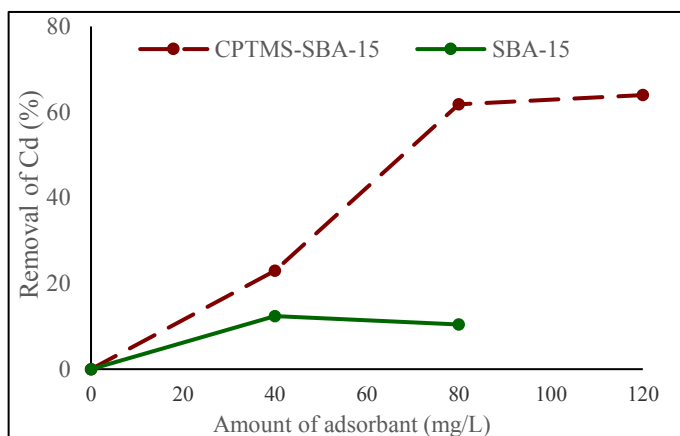


Fig. 9. Effect of amount of adsorbant on cadmium removal

3.3 Adsorption of Zn and Cadmium

The result of adsorption of Zinc can be seen in figure 10. It shows that as the concentration of SBA-15 was increased, the removal capacity becomes lower. According to figure 10, in the case of SBA-15, the percentage of removal at 60 mg/L of Zn is 44.67% and the highest concentration of Zn is at 140 mg/L with the percentage of removal 7.8%. In the other hand, for CPTMS-SBA-15, the result of percentage of removal at 60 mg/L for Zn is 11% and at 140 mg/L of Zn is 6.5%. It can be observed that the removal efficiency of CPTMS-SBA-15 is lower than SBA-15.

The removal efficiency of Cd^{2+} were carried out by Cd^{2+} ion adsorption test. The investigation of Cd removal has been observed by measuring the initial and final concentration of Cd ion. Based on the results of Cd adsorption test, the Cd initial concentration at 50 ppm has the highest removal percentage 60%. The increasing of Cd initial concentration will be followed by the decreasing of adsorption removal percentage. It's due to the increasing of heavy metal concentration is not proportional to the increase of amount of SBA-15.

The lower efficiency in Zn adsorption system may be due to the larger differences of electronegativity between Chlor and Zn in comparison with the Chlor and Cd system. The surface of SBA-15 was modified by CPTMS and causing chlor attach in the end of bond of SBA-15.

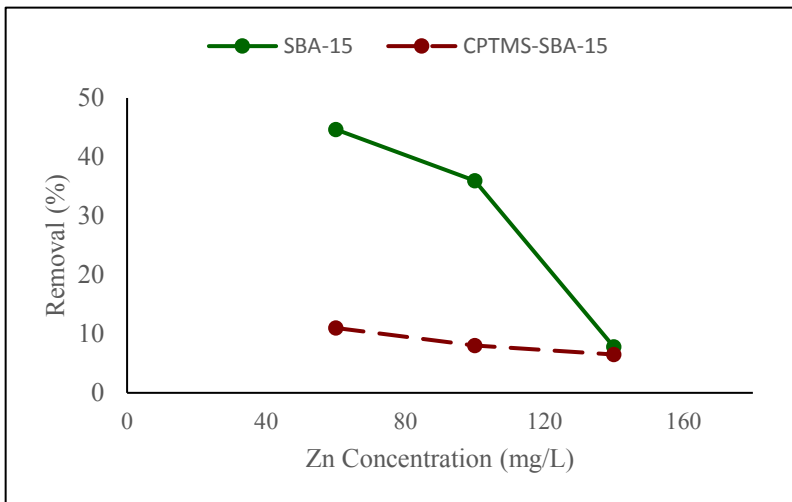
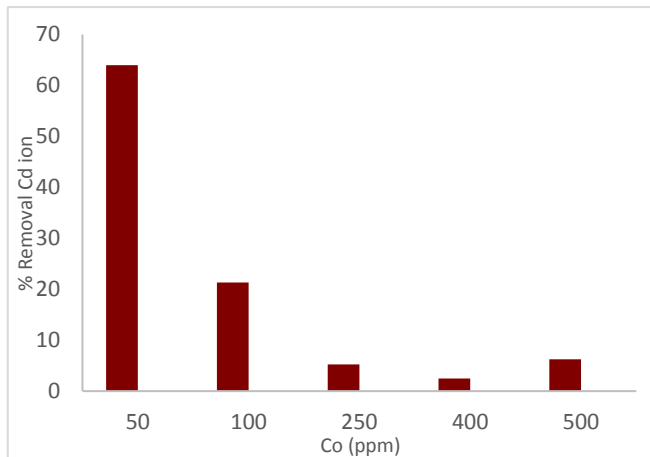


Fig. 10. The comparison of initial concentration on Zn removal

Table 2. The comparison of initial concentration on Cd removal



4 Conclusion

SBA-15 has been successfully synthesized with TEOS and Pluronic P123[®] then functionalized with CPTMS. SBA-15 pores is hexagonal structure. The functionalization reduced specific area, diameter pore and volume. This is occur because inside the pores and on the surface has a chlor ion. Zinc as heavy metal samples has lower efficiency of adsorption with CPTMS-SBA-15 than Cd. It may be due to the differences of electronegativity between Zn and Chlor is higher in comparison with the Cd and Chlor system. It caused Zn was merely attached to the surface of CPTMS-SBA-15 while on the other hand Cd is able to be adsorb properly throughout the pore of adsorbant. Due to its smaller pore size and also surface area, it was strengthened the fact that CPTMS-SBA-15 has lower adsorbtion properties of Zn.

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