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Preparation of Silica Modified with 2-Mercaptoimidazole and its Sorption Properties of Chromium(III)

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Abstract: Modified silica gel was prepared to remove the heavy metal of chromium(III) from water sample. Silica gel was used as supporting material and the 2-mercaptoimidazole was immobilized onto surface silica so that the silica would have selective properties to adsorb the heavy metal chromium(III) through the formation of coordination compound between the 2-mercaptoimidazole and chromium(III). The characterization of modified silica gel was carried out by analyzing the Fourier Transform Infrared Spectrum of this material in order to ensure the immobilization of 2-mercaptoimidazole onto the surface. The effect of pH solution, initial concentration of chromium(III), and interaction time were investigated in batch mode to find the adsorption properties of chromium(III) onto modified silica. The condition optimum of these parameters was applied to determine the removal percentage of chromium(III) in water sample using the modified silica gel.

Keywords: Heavy metal, Chromium(III), Adsorption, Silica, 2-Mercaptoimidazole

Introduction

Nowadays, the heavy metal pollution has become big problem in the world since the heavy metal in particular concentration can affect to the human and organism body. Heavy metal in trace concentration is extremely needed by life process for instance the human body need some minerals to support the metabolism process. However, heavy metal in high concentration can cause illness or poisonous for human such as dysfunction of nerve system, blood composition changing, heart and lungs disease, *etc.* For example, the excessive exposure and inhalation of chromium can cause various diseases and damage the liver, kidney, circulatory system, nerve tissue, and blood forming organs¹. Therefore, analytical method and separation technology has been developed to identify the heavy metal pollution in recent days.

Several techniques can be used for separation and preconcentration of trace heavy metal such as liquid-liquid extraction, solid phase extraction, coprecipitation, ion exchange, floatation, and electrochemistry deposition^{2,3}. Solid phase extraction is the most frequently technique used for separation and preconcentration of heavy metal because it unnecessary to use the dangerous solvent. In this technique, many materials are used as adsorbent such as polymer resin, porous glass silica, and silica modified by grafting or sol gel method⁴. For analytical purposes, silica modified by organic functional group is commonly used since the material silica provides many advantages such as inert, good adsorption and cation exchange capacity, easy to prepare with chemical compound and particular impregnate medium to create several of modified silica surface, high mechanic and thermal stability. In addition, the retention processes of analyte (adsorption, ion exchange, chelate complex formation) on silica surface is reversible so that the silica adsorbent could be used for preconcentration and separation^{5,6}.

The modification of silica by organic functional group could enhance the adsorption and ion exchange capability of silica gel so that it has good selectivity for metal ions. Chemical compounds contained donor atom such as sulfur, nitrogen, phosphor, oxygen are commonly used to modify silica surface. There are two processes to immobilization the organic functional group onto silica surface such as chemical adsorption and physical adsorption. In chemical adsorption, the donor atom of organic compound chemically bonded with amine or chloro group attached on silica surface. Meanwhile, in physical adsorption, the organic functional groups physically adsorbed onto silica surface⁵.

Since modified silica has high surface area and high mechanical stability, it usually uses for catalysis application. In the other hand, modified silica gel also can be used for precocentration and separation of trace metal before on line precocentration analysis with flow injection flame Atomic Absorption Spectrometry (AAS), spectrophotometry, potentiometry and electrochemistry, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)^{2,7-9}. The use of modified silica with organic functional group has become the interesting research object at the moment⁵. Some organic compound has been used to modify silica gel for heavy metal removal purposes such as 5-formyl(1-carboxyphenyazo)salicylic acid, 8-hydroxyquinoline, tetra(2-aminoethyl)-ethylenediamine, 3-methyl-1-phenyl-5-pyrazone, 1,8-dihydroxyanthraquinone, dihydroxybenzen, 1,10-phenanthroline, 1-(2-thiazolyazo)-2-naphthol, 1,5-bis(di-2-pyridil)methylenethiocarbohydrazide, 2-[2-(6-methyl-benzothiazolyazo)-4-bromophenol]^{10,11}.

This article describes modified silica with 2-mercaptoimidazole. Activated silica gel was modified first with 3-chloropropyltrimethoxysilane to load the chlor group which will bond with the organic functional group contained in 2-mercaptoimidazole. Then the sorption behavior of chromium(III) in modified silica has been investigated. The modified silica with 2-mercaptoimidazole was applied to remove the chromium(III) from the water sample.

Experimental

Chemicals and reagents

The chemicals are pro analysis grade consist of Silica gel, 3-chloropropyltrimethoxysilane, 2-mercaptoimidazole, chrom(III) nitrate nonahydrate, sodium hydrogenphosphat, citric acid, ethanol, toluene, sodium sulfate anhydrous, demineralized water, nitrogen gas flow, hydrochloric acid.

Instruments

Reflux apparatus for preparing the silica modified. Shaker Micromat for shaking the silica modified in chromium(III) solution. Vacuum oven for drying the silica modified. Fourier

Transform Infrared Spectrometer (FT-IR) Shimadzu for characterization of silica modified. Meanwhile, Graphite Furnace Atomic Absorption Spectrometer SpectrAA-880 Zeeman Varian measured chromium(III) remained in solution.

Preparation of silica modified with 2-mercaptoimidazole

Silica activated

10 g of silica gel was immersed in 50 mL hydrochloric acid of 4 M. This mixture was allowed to reflux with stirring for 4 h. Then, it was filtered and washed with demineralized water until acid free. The silica was dried in furnace 150°C for 5 h. Silica activated was characterized by Fourier Transform Infrared Spectrometry.

Silica loaded with 3-chloropropyltrimethoxysilane (Si-CTS)

1 g of activated silica was mixed with 20 mL dry toluene and 2.5 mL 3-chloropropyl trimethoxysilane. The mixture was refluxed at 70-80°C with stirring for 8 h. Then, it was filtered and washed with dry toluene, and dry acetone. The Si-CTS was dried in vacuum oven at 70°C for 3 h. Si-CTS was characterized by Fourier Transform Infrared Spectrometry.

Si-CTS modified 2-mercaptoimidazole (Si-CTS-MCP)

40 mL of dry toluene and 5 mL of 4% (v/v) 2-mercaptoimidazole solution was added into 1 g of Si-CTS. The mixture was allowed to reflux at 70-80°C under nitrogen flow condition for 8 h. Modified silica was filtered and washed with toluene to remove 2-mercaptoimidazole unattached into silica. Finally, it was dried in oven vacuum at 50°C for 3 h. Si-CTS-MCP was characterized by Fourier Transform Infrared Spectrometry.

Sorption behavior of chromium(III) on silica modified

Stock solution of chromium(III) 1000 mg/L

0.777 g of chrom(III) nitrate nonahydrate was dissolved in 100 mL of demineralized water.

Effect of pH

Solution of chromium(III) with concentration of 5 mg/L was prepared from dilution of stock solution of chromium(III) in 1000 mg/L. 50 mg of investigated adsorbent (Si-CTS-MCP) was suspended with constant shaking for one hour in 10 mL of 5 mg/L chromium(III) solution at desired pH with range (2-10). The solution was filtered, and then the filtrate was analyzed by atomic absorption spectrometry for the amount of chromium(III) being adsorbed.

Effect of initial concentration

After the pH optimum for adsorption of chromium in investigated silica was found, 50 mg of Si-CTS-MCP was immersed and allowed to shake for one hour in 10 mL of various concentrations chromium(III) solution (0.5-200 mg/L) at pH optimum. The solution was filtered. Then, the concentration of chromium(III) contained in the filtrate was determined by atomic absorption spectrometry. The quantity of chromium(III) adsorbed by 1 g of adsorbent is commonly called the metal ion adsorption capacity "a". The "a" value can be calculated with formula as described below⁴.

$$\alpha = \frac{(C_0 - C_1)}{m} \times V$$

Where, a is the metal ion adsorption capacity (mg/g adsorbent), C_o is the initial concentration of metal ion (mg/L), C_1 is the metal ion concentration at the equilibrium found in the solution (mg/L), m is the mass of adsorbent (g), and V is total volume of solution (mL)

Effect of interaction time

50 mg of Si-CTS-MCP was immersed in 10 mL of 5 mg/L chromium(III) solution (0.5-200 mg/L) at pH optimum and allowed to shake for different periods (0-80 min). The solution was filtered, and then the filtrate was analyzed by atomic absorption spectrometry for the amount of chromium(III) being adsorbed.

Separation of Chromium(III) from water sample by modified silica

10 mL of water sample was added with 5 mg/L of chromium(III) solution. Then 50 mg of Si-CTS-MCP was suspended with constant shaking in 10 mL of water sample at pH and shaking time optimum. The concentration of chromium(III) contained in the supernatant was determined by atomic absorption spectrometry to investigate the amount of chromium(III) adsorbed onto Si-CTS-MCP. The % removal of chromium(III) by Si-CTS-MCP was calculated with the following formula:

$$\% \text{ Removal of chromium(III)} = \frac{[\text{Chromium(III) adsorption}]}{[\text{Chromium(III) initial}]} \times 100\%$$

Result and Discussion

Preparation of silica modified with 2-mercaptoimidazole

Characterization of activated silica

The Fourier Transform Infrared (FT-IR) spectrum of activated silica shown in Figure 1. The silanol group was observed by the presence of -OH stretch at 3207.62 cm⁻¹, 3479.62 cm⁻¹ bands, while the siloksan (Si-O-Si) groups was observed at 1107.14 cm⁻¹ band. Both of those groups are responsible as active site of silica gel which can be modified.

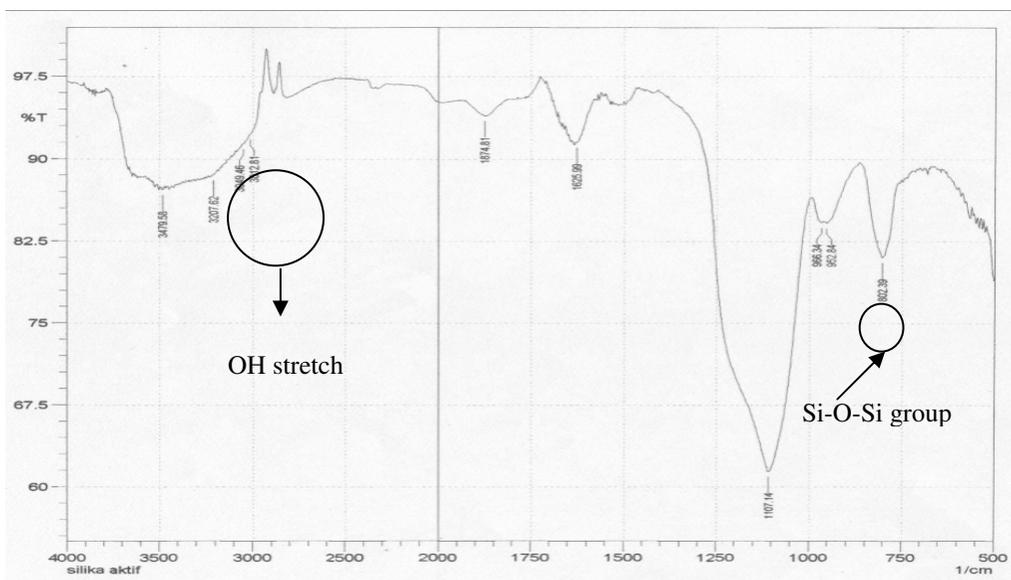


Figure 1. FT-IR spectrum of activated silica.

The silica has to be activated first before modification process with organic functional group. In the activation of silica, silica was immersed in hydrochloric acid solution to remove the trace metal¹² and dried in 150°C for 3 h to evaporate the water molecules which bonded in silanol group (Si-OH) through hydrogen bonding so that the silanol groups can form covalent bond with the functional groups of compound¹³. In the other hand, the loss of water molecule from silica caused the bigger surface area and the pore of silica so that physical adsorption, chemical adsorption, and capillary condensation process become more efficient and effective. The scheme of activated silica was shown in Figure 2.

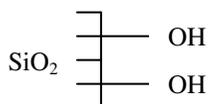


Figure 2. Scheme of activated silica⁵.

Characterization of Si-CTS

Characterization of Si-CTS with FT-IR showed the presence of aliphatic C-H stretch at 2958.80 cm⁻¹ band, C-H bend at 1442.75 cm⁻¹ and 1408.04 cm⁻¹ bands which are corresponding to 3-chloropropyltrimethoxysilane, as shown in Figure 3.

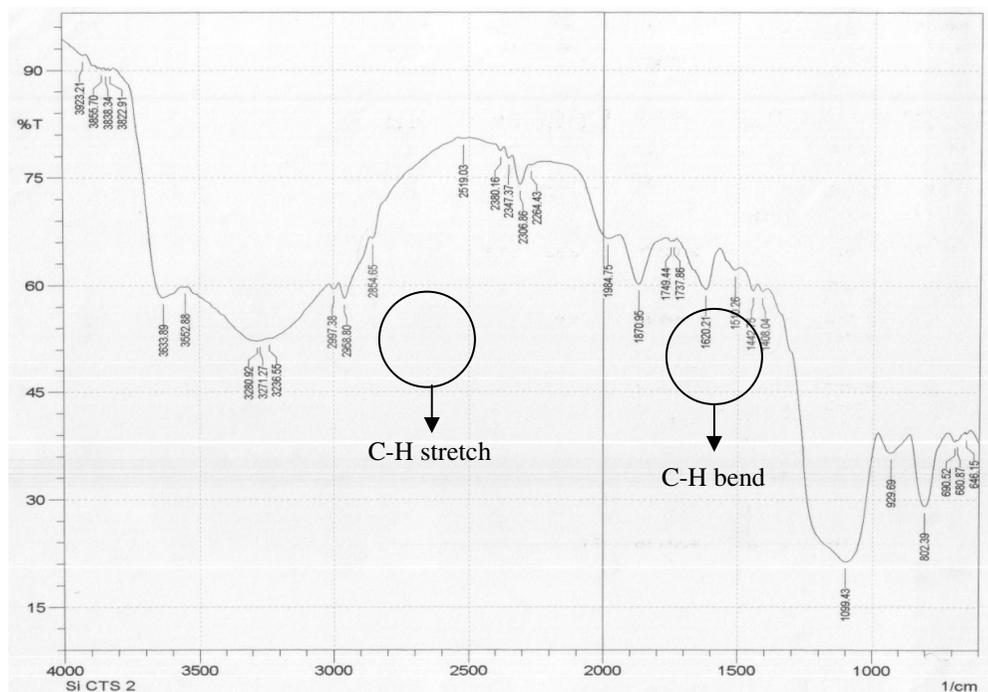


Figure 3. FT-IR spectrum of Si-CTS.

Silica activated was modified with 3-chloropropyltrimethoxysilane to attach chlor group into silica before immobilization with 2-mercaptoimidazole^{16,17}. Furthermore, 3-chloropropyltrimethoxysilane was important needed as intermediate reagent to immobilize heterocyclic compound such as 2-mercaptoimidazole into silica surface¹⁴. The scheme of Si-CTS was shown in Figure 4.

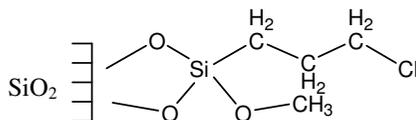


Figure 4. Scheme of Si-CTS⁵.

Characterization of Si-CTS-MCP

Modification of Si-CTS with 2-mercaptoimidazole ligand showed that the ligand was successfully immobilized to silica. The S-H stretch at 2630 cm^{-1} , N-H bend at 1585 cm^{-1} , C-S stretch at 673.16 cm^{-1} , and C=C stretch at 3128.54 cm^{-1} can be observed from the IR spectrum of Si-CTS-MCP¹⁵, as shown in Figure 5.

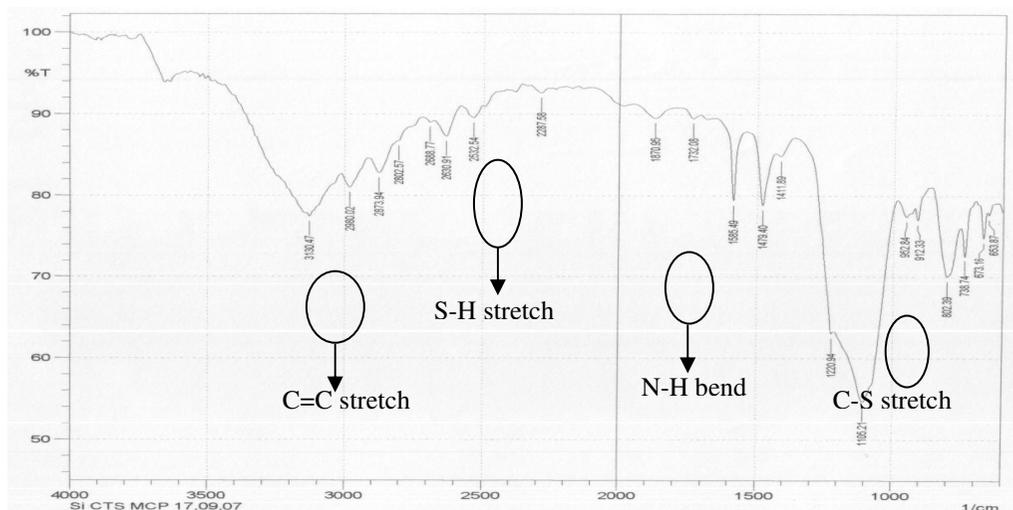


Figure 5. FT-IR spectrum of Si-CTS-MCP.

2-Mercaptoimidazole ligand can be immobilized to the silica because the nucleophilic substitution reaction mechanism ($\text{S}_{\text{N}}2$) occurred between the chlor group from 3-chloropropyltrimethoxysilane and 2-mercaptoimidazole¹⁴. The scheme of Si-CTS-MCP was described in Figure 6.

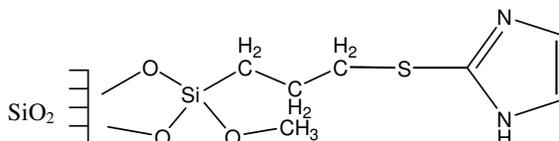


Figure 6. Scheme of Si-CTS-MCP⁵.

Sorption behavior of Chromium(III) on Si-CTS-MCP

Effect of pH

Metal adsorption on silica modified with organic ligand occurred through the formation of coordination compound between metal ion and donor atom in organic ligand. Therefore, pH of solution is one of the most important parameter which effect to the concentration of metal adsorbed on the silica modified¹⁷. The % of chromium(III) adsorbed on Si-CTS-MCP and activated silica in various condition of pH (2-10) was described in Figure 7.

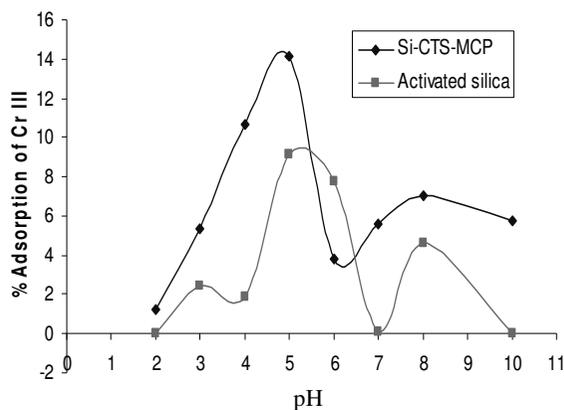


Figure 7. Effect of pH solution on percentage of chromium(III) adsorbed onto Si-CTS-MCP and activated silica.

Figure 7 showed that adsorption of chromium(III) gained optimum condition at pH 5. Si-CTS-MCP can adsorb 14,151% of chromium(III) while 9,106% of chromium(III) can only be adsorbed by activated silica at particular pH. Moreover, the percentage adsorption of chromium(III) was increased from the pH value 2-5. This indicated that the increasing of pH caused deprotonation of nitrogen atom in 2-mercaptoimidazole so that chromium(III) might form the coordination compound through two atom donors which is nitrogen and sulphur¹⁸, as described in Figure 8.

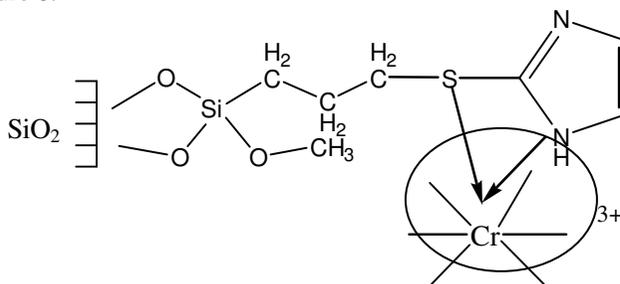


Figure 8. Scheme of the formation of coordination compound between chromium(III) and Si-CTS-MCP

Sulphur atom only roled as donor atom in forming covalent coordination bond at lower pH (pH 2)¹⁸. Meanwhile at higher pH (pH 5) there is two atom donors such as nitrogen and sulphur in the formation of covalent coordination bond with ion metal so that more ions of chromium(III) attached onto silica modified with MCP than at lower pH. The adsorption of chromium(III) onto Si-CTS-MCP decreased at pH higher than 5, as shown in Figure 5, because the presence of more ion OH^- at pH closely to 14 responsible for the formation of chromium(III) coordination compound as hydroxyl complexes $\text{Cr}(\text{OH})_3$ which was remained in solution¹⁷.

Effect of initial concentration chromium(III)

The interaction of various concentration of chromium(III) (5-250 mg/L) onto adsorbent Si-CTS-MCP and activated silica was carried out in pH optimum 5 for 1 h to determine the metal ion adsorption capacity, as shown in Figure 9.

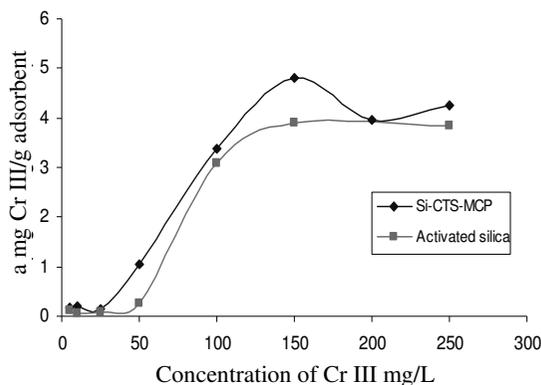


Figure 9. Effect of the initial concentration of chromium(III) on adsorption of chromium(III) onto 1 g of Si-CTS-MCP and activated silica.

Figure 9 described that the amount of chromium(III) adsorbed onto Si-CTS-MCP increased along with the increasing of the concentration of chromium(III) from 5 mg/L until 150 mg/L. The increasing of concentration of chromium(III) caused more ion chromium(III) in solution which interacted and attached to the active site of the Si-CTS-MCP through the formation of covalent coordination bond between the ion chromium(III) and mercaptoimidazole. However, the number of active site in Si-CTS-MCP is constant at the fixed amount of adsorbent¹⁷, so the amount of chromium(III) would be constantly adsorbed onto Si-CTS-MCP in particular concentration of chromium(III). It is shown in Figure 9, the adsorption capacity of chromium(III) tend to constant at the initial concentration of chromium(III) higher than 150 mg/L which was indicated with the plateau graphic. It means that the whole active site in Si-CTS-MCP was fully attached by chromium(III).

Effect of the interaction time (shaking time)

In addition to pH, the other factor effecting to the adsorption of chromium(III) onto Si-CTS_MCP is the interaction time of chromium(III) to reach the equilibrium with the Si-CTS-MCP. Figure 10 showed the amount of chromium(III) adsorbed onto Si-CTS-MCP in the various condition of interaction time where the experimental set in optimum pH 5, and 5 mg/L of chromium(III) as initial concentration. The percentage adsorption of chromium(III) onto Si-CTS-MCP increased from 0% at 0 min until 16,068% at 80 min.

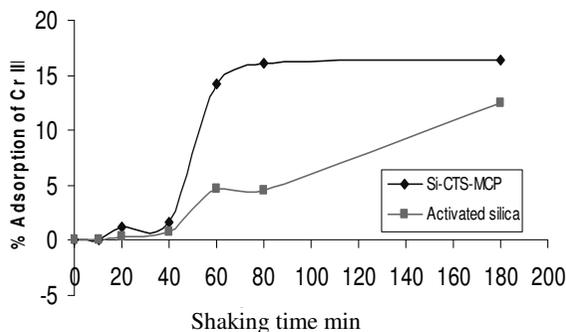


Figure 10. Effect of the interaction time on the percentage adsorption of chromium(III) onto Si-CTS-MCP and activated silica.

However, from Figure 10, the amount of chromium(III) adsorbed by Si-CTS-MCP tend to constant at the interaction time higher than 80 min which was shown the plateau graph starting at 80 min till 180 min. This indicated that the whole active sites of Si-CTS-MCP reached the equilibrium with the chromium(III) in solution so that Si-CTS-MCP cannot adsorb more ions chromium(III) in solution though the interaction time between chromium(III) and adsorbent was set longer than 80 min.

Separation of Chromium(III) from water sample by modified silica

After the condition optimum of adsorption of chromium(III) onto Si-CTS-MCP had been determined, the Si-CTS-MCP was applied to remove the chromium(III) from the water sample. The water sample contained 5 mg/L of chromium(III) was interacted with the Si-CTS-MCP at pH solution 5 for 80 min. Table 1 showed that Si-CTS-MCP was able to remove 16.067% of chromium(III) from water sample.

Table 1. Percentage removal of Chromium(III) in water sample.

Replicates	[Chromium(III)], mg/L		% Removal of chromium(III)	Mean % removal of chromium(III)	σ
	Initial	Adsorption			
1	5.280	0.805	15.246	16.067	1.160
2	5.300	0.895	16.887		

Conclusion

The organic ligand 2-mercaptoimidazole was successfully immobilized onto silica through the reaction with 3-chloropropyltrimethoxysilane as intermediate reagent. This modified silica (Si-CTS-MCP) can optimally adsorb chromium(III) in pH solution 5 and interaction time 80 min. It also can be interacted with the concentration of chromium(III) until 150 mg/L. When the modified silica was applied to remove chromium(III) from water sample, 16.067 % of chromium(III) could be adsorbed by Si-CTS-MCP in optimum condition.

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