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Adsorption of Chromium (VI) with Silica Coated on Iron Sand Magnetic Material Modified with Propyldiethylenetriamine

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ABSTRACT

Chromium metal ions with an oxidation number of six (Cr (VI)) were heavy metals that are toxic and harmful to the environment that pollute the environment from industrial waste, so efforts are needed to overcome the metal ion waste. In this study has been tested a silica coated on iron sand magnetic material modified with propyldiethylenetriamine to adsorb heavy metal of Cr (VI) on pH variation, adsorbate concentration variation, and time variation. The research was started with the preparation of iron sand magnetic material with an external magnet, activation of iron sand magnetic material with HCl solution, silica coating by propyldiethylenetriamine group on the batch system, silica-propyldiethylenetriamine coating on iron sand magnetic material using sol-gel method, and adsorption process to Cr (VI) was performed at pH variation 5–7, adsorbate concentration 200-500 ppm, and contact time 30–180 min. The results showed that the adsorbent of silica coated on iron sand magnetic material modified with propyldiethylenetriamine made capable of adsorption Cr (VI). The optimum condition of adsorption occurs at pH 6, contact time 60 min with a concentration of Cr (VI) at 400 ppm. At optimum conditions, adsorbent of silica coated on iron sand magnetic material modified with propyldiethylenetriamine has the ability to adsorb metal ions chromium (VI) of 81.09% with adsorbed 324.34 ppm from initial concentration 400 ppm..

Keywords: adsorbent, chromium (VI), iron sand, propyldiethylenetriamine.

1. INTRODUCTION

Heavy metals pose a significant threat to both the environment and human health due to their non-biodegradable nature, tendency to accumulate in the human body, and ability to disrupt the existence of aquatic creatures [1]. Chromium metal (Cr) is classified as a heavy metal because it has a density of more than 5 g/cm^3 which is 7.19 g/cm^3 [2]. Cr metal ions in the form of Cr(VI) are toxic, mutagenic, and carcinogenic [3,4]. Cr(VI) metal ions that pollute the environment usually come from chemical industry waste discharges, electroplating industries, tanneries, and the pigment industry [5,6]. The Cr (VI) content of 21.86 ppm in electroplating waste must be lowered to the maximum Cr (VI) threshold of 0.1 ppm based on regulation of the Minister of Environment No. 5 of 2014 [7]. This has become one of the main problems in the field of environment [8]. Therefore, an appropriate method was needed to overcome the Cr(VI) heavy metal ion waste so as not to pollute the environment continuously.

Several research methods have been conducted to overcome the Cr(VI) metal ions, among others, electrocoagulation methods, photocatalytic reduction, reducing bacteria [9], ion exchange [10], precipitation [11], osmosis [12], and membranes [13]. However, these methods have some disadvantages among others, it takes a lot of reagents, high energy, incomplete metal removal, and produces secondary waste [14]. Another alternative method that can be used is the adsorption method [15]. The adsorption

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approach has several benefits over other ecologically friendly methods. It requires minimal use of solvents, does not generate hazardous waste, inexpensive, and capplicable to low concentrations of metal ions. Additionally, it allows for reuse of adsorbent [16,17].

Research on the adsorption of Cr(VI) metal ions has been widely conducted using biosorbents made from chitosan [18], *Bacillus sp. Strains of* CRB-B1 [19], fungal biomass [4], *Bacillus amyloliquefaciens* [20], and *Bacillus sp* [21]. However, the biosorbent has disadvantages such as small size, low specific gravity, the structure is easily damaged because it is decomposed by other microorganisms, difficult to use in the column, and easily subjected to lysis in acidic conditions, and its limited adsorption capacity [22]. Another adsorbent alternative that can be used is silica gel, which has active groups in the form of silanol (Si-OH) and siloxane (Si-O-Si) [8]. Silica gel has a flexible structure, resistance to heat, good mechanical stability, and a large surface area [23]. Another advantage of silica gel as an adsorbent is its modifiable surface with organic or inorganic functional groups to improve the effectiveness and selectivity of adsorption of metal ions [24]. The surface of silica gel can be modified with functional groups such as -CN, -SH, and -NH_2 [25-27].

The amine (-NH_2) group produced better coverage and stronger intensity of adsorption bands than the mercapto Group [28]. According to Hamoudi et al. [29] the greater the number of amine groups used to coat the silica surface, the greater the adsorption capacity produced, adsorbents modified with mono-, di-, and tri- amine functional groups respectively produce adsorption capabilities of 0.80; 1.16; and 1.38 mmol NO_3^-/g adsorbent. To improve the ability to adsorb heavy metal ions Cr(VI), then in this study organic compounds with three amine groups of the reagent silane N-3-(Trimethoxysilylpropyl) diethylenetri-amine was used to modify the surface of silica.

The difficulty of separating the adsorbent from the solution becomes an obstacle in the process of adsorption on the batch system. In order to simplify the process of removing the adsorbent from the solution system, it is necessary to modify the adsorbent by including magnetic materials [30]. The adsorbent in this study was modified with magnetic material from iron sand to facilitate the separation of the adsorbent from the solution using the help of external magnets. Iron sand is found along the coast. In Indonesia, as much as 16,876,815 tons of iron sand are found along the northern and southern coasts of Central Java such as Jepara, Purworejo, Cilacap, Kebumen, and Kendal. One of the beaches in Kendal Regency that has iron sand is Pidodo Kulon Village Beach. Iron sand should be washed using an acid solution to remove impurity oxides such as MgO, Al_2O_3, SiO_2, CaO, and others [31]. In this study, magnetic material washing of Kendal Beach iron sand using HCl solutions, which is then coated by silica-triamine using the sol-gel process [32].

The amount of initial concentration of the solution, pH, and contact time are very important parameters in the adsorption process that will determine the amount of adsorbed metal ions and the optimum condition of adsorption [33]. This study investigated the performance of silica coated on iron sand magnetic material modified with propyldiethylenetriamine to adsorb Cr(VI) metal ions on a laboratory scale at pH variation, adsorbate concentration variation, and adsorption time variation

2. RESEARCH METHODS

2.1. Material

Iron sand with Fe 81.66% was obtained from Kendal Regency of Central Java, Indonesia as source magnetic material [30]. Sodium Chloride (HCl, 37%), Potassium Chromate (K_2CrO_4), Potassium Hydrogen Phthalate ($C_8H_5KO_4$), and Sodium Silicate (Na_2SiO_3 with SiO_2 25,5-28,5%) were purchased from Merck. N–(3–Trimethoxysilylpropyl) diethylenetriamine (TMSPDETA, 99%), and

Sodium citrate dihydrate (99%) were purchased from Sigma-Aldrich.

2.2. Syhthesis of Adsorbent Material

The preparation of adsorbent material of silica coated on iron sand magnetic material modified with propyldiethylene-triamine (MM@SiO_2@PDETA) refers to the method carried out by previous studies [30]. Briefly, 5 g of iron sand magnetic material was soaked with distillation water,then it was sonicated for 30 min. Step was repeated up to 3 times. Then the iron sand magnetic material is washed with 10 mL of HCl 1 M solution while dissonating for 30 min, then it was washed with distillation water until the pH is neutral. Next, the iron sand magnetic material was soaked in 100 mL of sodium citrate solution for 24 h. Iron sand magnetic material Iron Sand was separated from the solution by an external magnet and oven-dried at 80 °C for 24 h.

The magnetic material of iron sand preparation was equipped with a modified silicon triamine group through a sol-gel approach. A total of 3 g of iron sand magnetic material was acidified with 1 mL of HCl 1 M solution. Then the iron sand magnetic material was added to a mixture of 3 mL of Na_2SiO_3 solution, 1.2 mL of distillation water, and 1.8 mL of N-(3-Trimethoxy-silylpropyl)diethylenetriamine which had been sonicated for 30 min. Furthermore, the mixture was sonicated for 30 min while dripping HCl solution 1 M to form a gel at pH 7. The gelled mixture is thenheated at 80 °C for 24 h at atmosphere pressure. After the aging process, washing was carried out with distilled water until the pH was neutral. The material was then characterized by Fourier Transform Infrared Spectrophotometer (FTIR, Shimadzu Prestige 21) to identify the functional groups of the material and characterized by X-Ray Diffractometer (XRD, Shimadzu XRD-600) for identification of mineral types of materials.

2.3. Peformance Test of Adsorbent material for Adsorption of Cr (VI)

Silica coated on iron sand magnetic material modified with propyldiethylenetriamine (MM@SiO_2@PDETA) as adsorbent was placed in plastic bottles of 10 mg each. Each adsorption process was carried out on a batch system using 10 mL of $K_2Cr_2O_7$ solution. In the variation of pH, adsorption was conducted on $K_2Cr_2O_7$ solution concentration 400 ppm at pH 5; 6; and 7 with an adsorption process for 60 min.

At various times, adsorption was carried out on a solution of $K_2Cr_2O_7$ concentration 400 ppm with optimum pH with varying adsorption times (60; 90; 150; 180) min. In concentration variation, adsorption was done on $K_2Cr_2O_7$ solution with concentration variation (200, 300, 400, 500) ppm with optimum pH and optimum adsorption time. After the adsorption process, the filtrate was characterized by an Atomic Absorption spectrophotometer (AAS, Perkin Elmer AA 3110) to determine the levels of adsorbed Cr(VI) metal ions, while the adsorbent solids were characterized by XRD to determine the presence of Cr(VI) metal ions in the adsorbent used for adsorption.

3. RESULTS AND DISCUSSION

3.1. Characteristic of Adsorbent Material

The adsorbent material of silica coated on iron sand magnetic material modified with propyldiethylenetriamine with label of (MM@SiO_2@PDETA) was characterized by FT-IR before of Cr (IV) metal ions. FTIR spectra results are shown in **Figure 1**. Prepared magnetic material spectra of iron sand in **Figure 1(a)** see characteristic peaks of magnetite characterized by the presence of Fe-O groups at the absorption peak of 590 cm^{-1} and presence of -OH groups at the absorption peak of 1638 cm^{-1} [34]. The presence of silica functional group of Si-O-Si at the absorption peak of 1031 cm^{-1} in iron sand is indicated that iron sand has impurity of SiO_2 [30].

On the otherhand, FTIR spectra of silica coated on magnetic material of iron sand modified with propyldiethylenetriamine was shown in **Figure 1(b)**. That FTIR spectra has significant differences, especially the absorption peak at 790 cm^{-1} which indicates the Si-O-Si stretched vibration symmetry and at 1080 cm^{-1} which indicates the Si-O-Si stretched vibration asymmetry [35]. In addition, there were absorption peak of 1552 cm^{-1} (N-H bending vibration), 1552 cm^{-1} (N-H bending vibration), 2865-2956 cm^{-1} (streching vibration asymetric and symetric of C-H), and 3443 cm^{-1} (N-H streching vibration) from the triamine group of propyldiethylenetriamine [36].

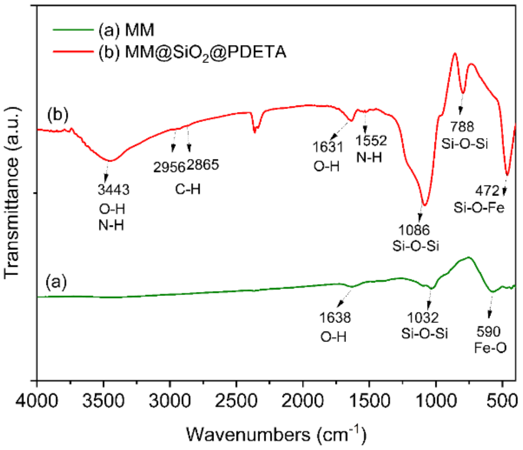

Figure 1. FTIR Spectra of a) prepared iron sand and b) silica coated on iron sand magnetic material modified with propyldiethylenetriamine

The next characteristic for the determination of crystal type in prepared iron sand magnetic material and silica coated on iron sand magnetic material modified with propyldiethylenetriamine is shown in **Figure 2.** Based on the diffraction pattern on the prepared iron sand magnetic material (**Figure 2.a**), the iron sand magnetic material has the characteristics of magnetite mineral according to JCPDS 19-0629 standard for Fe_3O_4 with the highest intensity peak on the crystal plane [220], [311], [400], [442], [511], [440] and the angle of 2ϴ is 30°, 35°, 42°, 53°, 56°, 62°. This is supported by research of Aghdasinia et al. [37]. In silica coated on iron sand magnetic material modified with propyldiethylenetriamine (**Figure 2.b**), in addition to having peaks of magnetite diffraction patterns with lower intensity also appears a widened peak between 20-26° indicating the presence of amorphous silica layer. This shows that the magnetic material of iron sand has been successfully coated by triamine-modified silica [30].

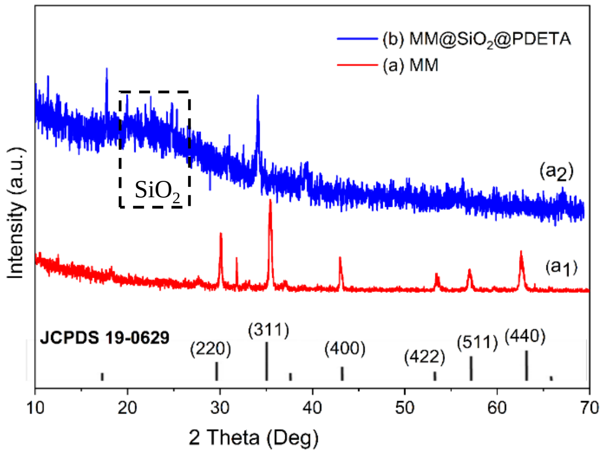

Figure 2. XRD pattern of (a) Prepared Iron Sand and (b) silica coated on iron sand magnetic material modified with propyldiethylenetriamine with JCPS 19-0629

3.2. Peformance of MM@SiO₂@PDETA as Adsorbent for Adsorption of Cr(VI)

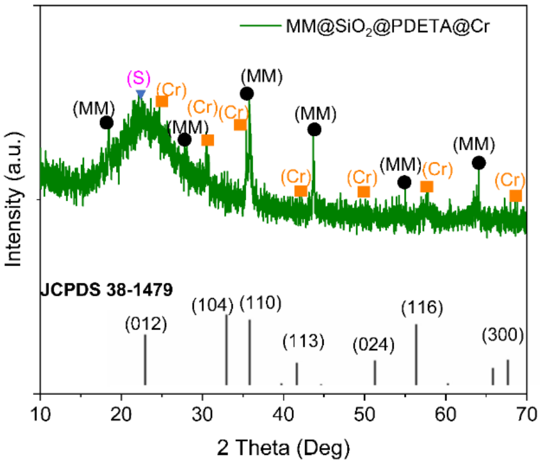

Figure 3. XRD pattern of silica coated on iron sand magnetic material modified with

propyldiethylenetriamine after Cr(VI) adsorption process with JCPDS 38-1479

In iron sand magnetic material was coated with triamine-modified silica after adsorption of chromium metal (**Figure 3**), in addition to having peaks of magnetite and silica diffraction patterns also appear peaks of chromium mineral peaks according to JCPDS 38-1479 standard for chromium Cr_2O_3 minerals in the crystal field [012], [104], [110], [113], [116], [300] with the angle of 2ϴ is 22°, 32°, 35°, 50°, 55°, 65°. This is supported by research [38]. It shows that the adsorbent material with magnetic material of iron sand coated with triamine-modified silica (MM@SiO_2@PDETA) has successfully adsorbed chromium ions with a Cr(VI) ion source and converted into Cr(III) ions in the form of Cr_2O_3.

3.2.1. Adsorption of Cr(VI) at pH Variation

The acidity level of the solution (pH) can affect the surface properties of the adsorbent, the molecular properties of the adsorbate, and the composition of the solution [1]. In pH variation, adsorption was done in a batch system by adding 10 ml of K_2CrO_7 solution at a concentration of 400 ppm with PH Variation (5, 6, and 7) in a container containing a modified silica adsorbent of propyldiethylenetriamine coated on a magnetic material of iron sand (MM@SiO_2@PDETA). The result of the adsorption of Cr (VI) on pH variation is shown in **Figure 4**.

Based on **Figure 4**, the triamine group-modified silica adsorbent coated on the iron sand magnetic material (MM@SiO_2@PDETA) can adsorb Cr(VI) at pH 5-7. This is because under acidic conditions, metal ions Cr(VI) which is dominated by the species $HCrO_4^-$ and $Cr_2O_7^{2-}$ have a negative charge, as stated by Dai et al. [18]. The relative distribution of the above Cr(VI) species depends on the pH of the solution, the concentration of Cr(VI), and the redox potential. Based Shen et al. [39], five main species of Cr(VI) exist, i.e., $Cr_2O_7^{2-}$, $HCr_2O_7^-$, CrO_4^{2-}, $HCrO_4^-$, and H_2CrO_4.

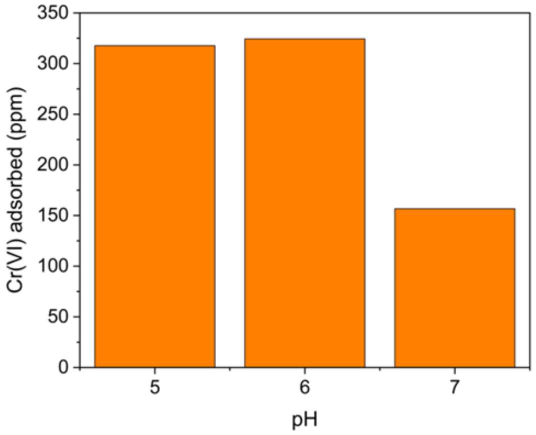

Figure 4. Effect of pH on the concentration of adsorbed Cr(VI) metal ions

While the amino group in the acid solution will react with H^+ to form $-NH_3^+$, so it can interact with the Cr(VI) anion. The bond that occurs between the adsorbent with Cr(VI) at acidic pH is an electrostatic bond that is between the protonated amino group ($-NH_3^+$) on the surface of the adsorbent with $HCrO_4^-$. In addition to electrostatic bonding, under acidic conditions, it is also possible to have hydrogen bonds between $HCrO_4^-$ and functional groups on the adsorbent surface ($-NH_3^+$ and Si-OH surface) [40].

Electrostatic forces and hydrogen bonds between the adsorbent and the $HCrO_4^-$ ion are effective factors in adsorption. Ionic strength can reduce the attractive force in two ways, namely neutralizing the negative charge on $HCrO_4^-$ and occupying the positive side of the adsorbent ($-NH_3^+$). In addition, reducing the adsorbent and adsorbate charges by sharing electrons can weaken the hydrogen bonds that occur. The strength of the attractive forces and hydrogen bonds that decrease will also reduce the amount of Cr(VI) metal ions that are adsorbed significantly as stated by Araghi et al. [41].

According to Etienne and Walcarius [42] the amine group will be protonated to ammonium at low pH, and according to Zhang et al. [43] at high pH, the amino group will interact with -OH forming $-NH^-$, while at low pH the amino group will be protonated to ($-NH_3^+$). According to Lam et al. [44] at low pH, the protonated $-NH_2$ group forming NH_3^+ as a Lewis acid can bind to a metal anion which is a Lewis base. At conditions above the zeta potential (pH>4), $-NH_2$ will tend as a Lewis base so that it can bind positively charged metal ions.

Based on **Figure 4**, it is known that the adsorption of Cr(VI) increases with the increasing pH of the solution from 5 to 6. The low adsorption value of Cr(VI) at pH 7. In addition, at pH>6, the triamine group at MM@SiO_2@PDETA which has a $-NH_2$ group tends to be a Lewis base so that it tends to bind metal cations to form electrostatic bonds as found by Lam et al. [44]. At pH>6, the metal ion Cr(VI) is in the form of CrO_4^{2-}. So that the bond that occurs between the triamine group from propyldiethylenetriamine at MM@SiO_2@PDETA with Cr(VI) metal ions tends to be chelated. A high pH means a decrease in the number of protons and a decrease in the interaction of amino groups with protons. As a result, the ionic interaction between the adsorbent and Cr(VI) decreases.

Adsorption results showed that the concentration of Cr(VI) metal ions was most widely adsorbed, occurred at pH 6 with the amount of adsorbed Cr metal ions as much as 324.34 ppm or about 81.09 % of the initial solution of 400 ppm. So it can be said that the optimum pH for adsorption of Cr(VI) metal ions by MM@SiO_2@PDETA occurs at pH 6. At pH 7 there is a decrease in the percentage of adsorbed Cr(VI) metal ions. It is possible that at that pH, the $-NH_2$ group cannot be protonated completely, causing the absorption of Cr(VI) metal ions to be reduced. This is consistent with the results of research by Dai et al. [18] and Araghi et al. [41] who said that the adsorption efficiency of Cr(VI) will decrease with increasing pH. This happens because at higher pH the protonation of the amino group is very low.

In this research, the adsorption of Cr(VI) is optimum at pH 6. The reaction of changing Cr (VI) to Cr(III) occurs in an acidic atmosphere between pH 2.0 and pH 6 with the following reaction [45]:

$$Cr_2O_7^{-2} + H_2O \rightarrow 2HCrO_4^-$$

$$2HCrO_4^- + H^+ + 3e^- \rightarrow 3Cr^{3+} + 4H_2O$$

This is supported by the results of XRD analysis that shows formed Cr(III) based on JCPDS 38-1479. The possible interactions that occur between Cr(VI) ions with adsorbent are as follows (**Figure 5**):

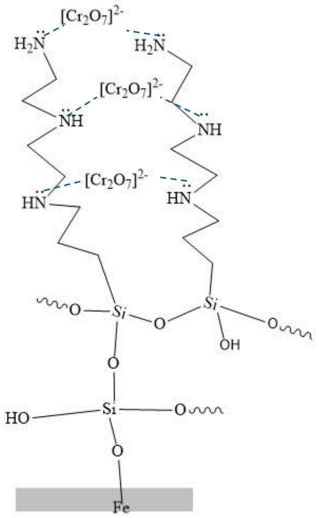

Figure 5. Possible interaction between $[Cr_2O_7]^{2-}$ with MM@SiO2@PDETA Adsorbent

3.2.2. Adsorption of Cr(VI) at Time Variation

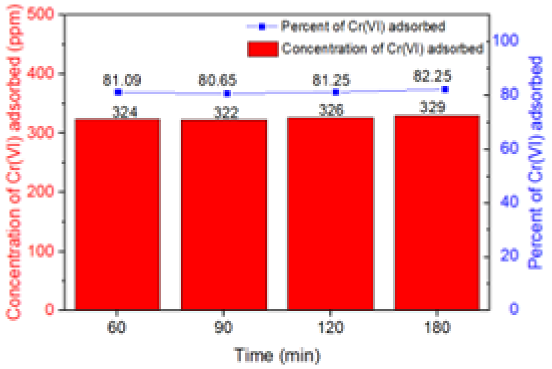

Figure 6. Concentration and persentase concentration of Cr(VI) metal ions adsorbed at optimum pH with initial concentration 400 ppm

In the variation of adsorption time, adsorption is done in a batch system by adding 10 ml of K_2CrO_7 solution with a concentration of 400 ppm, optimum pH 6, and time variation (60, 90, 120, 150, and 180 min) by modified silica adsorbent of triamine group coated on magnetic material of iron sand (MM@SiO2@PDETA). It aims to determine the minimum time to adsorb metal ions Cr(VI) to the maximum by the adsorbent made. The results of adsorption at time variations are shown in **Figure 6**.

Based on **Figure 6**, it can be seen that the concentration of Cr(VI) metal ions that are adsorbed the most is 329.01 ppm (82.25%) occurring at an adsorption time of 180 min. At the adsorption time of 60 min, the adsorbent can adsorb the concentration of Cr(VI) metal ions as much as 324.34 ppm (81.09%). When viewing the number of concentrations of Cr(VI) metal ions adsorbed, then the number of concentrations of Cr(VI) metal ions adsorbed at 60, 120, 150, and 180 min is not too significantly different. Although at 180 min it can adsorb the most Cr(VI) metal ions, the most effective adsorption time is at 60 min. The decrease in the concentration of rapidly adsorbed Cr(VI) metal ions at the beginning of the reaction is associated with a high surface concentration of $-NH_3^+$ groups and a strong interaction of $HCrO_4^-$ with the adsorbent. Adsorbed Cr(VI) decreased from 60 min to 90 min and increased from 90 min to 180 min. At 120-180, contact time does not give a significant difference, so it can be said that equilibrium has occurred after 120 to 180 min. Based on the description, it can be concluded that the effective time for adsorption of Cr(VI) is the contact time of 60 min.

3.2.3. Adsorption of Cr(VI) at Adsorbate Concentration Variation

In concentration variation, adsorption was done in a batch system with optimum pH 6 and effective time of 60 min by adding 10 ml of K_2CrO_7 solution with concentration variation (200, 300, 400, and 500 ppm) into plastic bottles containing modified silica adsorbent of triamine group coated on magnetic material of Kendal Beach iron sand (MM@SiO_2@PDETA). The results of adsorption at varying concentrations are shown in **Figure 7**. Based on **Figure 7**, it can be seen that there is a linear increase between the amount of Cr(VI) ions adsorbed with an increase in the initial concentration of Cr(VI) metal ions. The more Cr(VI) metal ions that had been added at initial concentration, the more of Cr(VI) was adsorbed by the absorbent MM@SiO_2@PDETA. This can be seen in concentration variations of 200 to 500 ppm.

The amount of adsorbed metal ions increased with the increase of the initial concentration used [6]. This is because the more Cr(VI) ions in the solution that can be adsorbed by the adsorbent MM@SiO_2@PDETA with increasing concentration of Cr(VI) solution. During these conditions, the transfer of Cr(VI) from the solution to the surface of the adsorbent occurs sharply, and it remains at the level of the equilibrium concentration of the solution to the adsorbed one. At higher concentrations of 500 ppm, the ability of adsorbents to adsorb Cr(VI) has decreased. The percentage of Cr(VI) metal ions adsorbed is 42.90%(214.51±2.65 ppm) from initial concentration of 500 ppm. It is possible on the surface of the adsorbent is full of metal ions Cr(VI), so the ability of the adsorbent is decreased. So that the concentration of Cr(VI) metal ions that are adsorbed is greatest in the concentration of Cr(VI) metal ions at 400 ppm which is 324.34±0.87 ppm (81.09%) of adsorbed Cr metal ions. This shows that the optimum conditions for the adsorption of Cr(VI) metal ions by MM@SiO_2@PDETA are at 400 ppm. According to research, the adsorbent MM@SiO_2@PDETA has the ability to absorb Cr(VI) metal ions by 81.09%. This ability is better compared to other adsorbents; for example, the adsorbent $CaFe_2O_4$@rGO@biochar has a Cr(VI) adsorption ability of 61.6% [46] and GO/PAMAM adsorbents have a Cr(VI) adsorption ability of 80.70% [47].

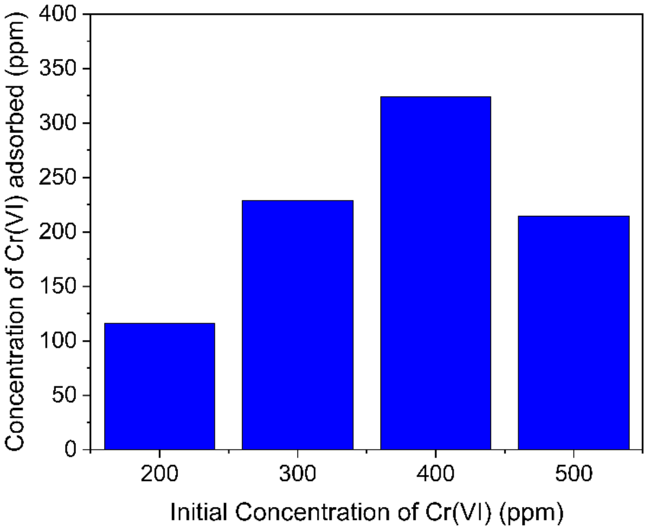

Figure 7. Effect of initial Cr(VI) metal ion concentration on Cr (VI) metal ion concentration adsorbed

4. CONCLUSION

Silica coated on iron sand magnetic material modified with propyldiethylenetriamine has been successfully synthesized by sol-gel approach from raw materials of natural iron sand, sodium silicate, and N-(3-Trimethoxysilylpropyl)diethylene triamine. The silica coated on iron sand magnetic material modified with propyldiethylene-triamine has successfully adsorbed chromium ions reaching 324.34 ppm (81.09%) with an optimum adsorption time of 60 min and an optimum pH of 6 by reducing Cr (VI) to Cr (III).

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