

CoFe₂O₄ Modified with *Polyethylene Glycol* (PEG) for Removal of Chromium (VI) Ion from Electroplating Wastewater

Poedji Loekitowati Hariani^{1,*}, Desnelli¹, Hermansyah¹, Salni²

¹Faculty of Health Sciences, Universiti Teknologi MARA, Selangor Malaysia

²Balochistan University of Information Technology, Engineering and Management Sciences, Quetta, Pakistan

³MAHSA University, Selangor, Malaysia

* Correspondent author: puji_lukitowati@mipa.unsri.ac.id

Received: October 14, 2017; Accepted: December 10, 2017

Abstract

One of the contaminants in the wastewater of the electroplating industry is Cr (VI). In this study, the magnetic adsorbent of CoFe₂O₄ which was coated with polyethylene glycol (PEG)-4000 was synthesized and used to removal of Cr (VI) from electroplating wastewater. The adsorbent obtained was characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Dispersive Energy X-Ray Spectrometer (EDS) and Vibrating Sample Magnetometer (VSM). The adsorption process was studied by the variable of the effects of the solution pH, contact time and weight of the adsorbent. Langmuir and Freundlich isotherm models were used to describe the interaction between the adsorbate and adsorbent. The kinetics and thermodynamics were used to determine the mechanism of adsorption. The results of the study showed that optimum condition for removal of Cr (VI) onto CoFe₂O₄ and CoFe₂O₄-PEG at pH 3 with contact time 35 minutes and weight of adsorbent 0.1 g. The adsorption process was in accordance with Langmuir's isotherm with maximum adsorption capacity using CoFe₂O₄ and CoFe₂O₄-PEG of 40.983 and 42.107 mg/g, respectively. The kinetics of the reaction of both adsorbents corresponded to the pseudo second-order. The value of the negative free energy (ΔG^0) indicated that the reaction occurred spontaneously. The efficiency for removal of Cr (VI) from the electroplating wastewater by CoFe₂O₄ and CoFe₂O₄-PEG was 68.48% and 73.39%, respectively.

Keywords; CoFe₂O₄, CoFe₂O₄-PEG, Cr (VI), electroplating wastewater

1. Introduction

Chromium (Cr) is one kind of heavy metals. Chromium is produced in great amount by such industries as tannins, metallurgy, textiles, paints, metal finishing and electroplating (Gurgel et al., 2009; Mohamed et al., 2017). Chromium in water exists in three forms of oxidation: divalent (II) chromium, trivalent (III) chromium and hexavalent (VI) chromium. Divalent (II) chromium is not stable, so in the environment only Cr (III) and Cr (VI) are often found. Cr (III) is an essential metal, required for the metabolism of fat and glucose in mammals, while Cr (VI) is toxic to biological systems, mutations in living organisms. Cr (VI) is suspected to be the cause of cancer. Cr (VI) has greater water solubility, mobile in nature and more bioavailable than Cr (III) (Kotas and Stasicka, 2000; Farooq et al., 2010; Pang et al., 2011). The form of chromium in water depends on the pH of the solution, in the natural waters in the form of CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, at a lower pH it is more dominant in the form of Cr (VI) is HCrO_4^- and at higher pH in the form CrO_4^{2-} (Gurgel et al., 2009; Ramos et al., 2008). Therefore, it is necessary to control industrial waste containing heavy metal ions especially Cr (VI) before it is discharged into the environment.

Various methods can be used to reduce Cr (VI) from liquid waste such as electrochemical through a reduction reaction of Cr (VI) to Cr (III) (Fang et al., 2012), chemical precipitation (Ramakrishnariah and Prathima, 2012), reduction, anion exchange, coagulation and filtration (Mc Guire et al., 2007), adsorption (Bishnoi et al., 2004). The adsorption method is considered to be the simplest, low cost, low energy and

efficient method for liquid waste treatment. Many adsorbents have been reported for the removal of Cr (VI) from a solution such as Fe_3O_4 (Ciftci and Ersoy, 2016; Ilankoon, 2014), nano fiber composite of PAN-CNT/ $\text{TiO}_2\text{-NH}_2$ (Mohamed et al., 2017), activated carbon (Rai et al., 2016; Kumar and Jena, 2017). The problem that occurs is how to improve the efficiency of adsorption and simplify the reused adsorbents (Foroughi et al., 2015).

At present, the research on magnetic materials as adsorbents continues to develop. Adsorbents are superparamagnetic, so they are easily separated from the solution after adsorption process using magnet without filtering or centrifugation and require a short time (Pang et al., 2011; Ciftci and Ersoy, 2016). One of the magnetic materials is Cobalt ferrite (CoFe_2O_4). The material has high coercivity, high saturation magnetization and chemical stability (Topkaya et al., 2013). The size of the material is small enough to cause frequent agglomeration. To reduce the agglomeration and to increase the adsorption capacity, the nanomagnetic material is composited with other materials. Some researchers have composited nanomagnetic materials with both organic and inorganic materials such as CuFe_2O_4 -activated carbon (Zhang et al., 2007), MnFe_2O_4 -Chitosan (Kim et al., 2010); Fe_2O_4 -activated carbon (Kakavandi et al., 2013), CoFe_2O_4 -graphene and NiFe_2O_4 -graphene (Santhosh et al., 2015), NiFe_2O_4 -activated carbon (Ranjeh et al., 2015), Fe_3O_4 -zeolite (Alswat et al., 2016).

In this study, nanomagnetic of CoFe_2O_4 was modified using an organic material, Polyethylene Glycol (PEG) and used to removal Cr (VI)

from electroplating wastewater. The combination with organic polymers is expected to increase flexibility, and to reduce agglomeration among nanoparticles. In addition, PEG also protects metal oxides from oxidation processes, has biocompatible and biodegradable properties. The main characteristic of electroplating wastewater is its heavy metal ions and its low pH. Therefore, electroplating wastewater needs to be treated before it is discharged into the environment. In this study, the synthesis of CoFe_2O_4 -PEG was performed using a co-precipitation method. The advantage of this method is that it is simple with a high success rate. The adsorbent generated was characterized using XRD, VSM, and SEM-EDS.

2. Materials and Methods

2.1 Chemicals

All reagents used have high purity, namely $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, PEG-4000, NaOH, HCl, $\text{K}_2\text{Cr}_2\text{O}_7$ from Merck. The wastewater of the electroplating industry comes from Palembang, South Sumatra, Indonesia.

2.2 Preparation of CoFe_2O_4 and CoFe_2O_4 -PEG

The synthesis of CoFe_2O_4 was carried out by mixing 5.406 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 2.379 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 25 mL deionized water. The mixture is stirred using a magnetic stirrer at 80°C , at a speed of 120 rpm for 1 hour while being flowed with N_2 . Furthermore, the addition of NaOH 1 M is done until the pH of the

solution ± 10 . Heating is continued for 1 hour to obtain a stable product. The resulting CoFe_2O_4 is in the form of black powder, separated from the solution using a permanent magnet. To remove the remaining reactants, the CoFe_2O_4 was washed using deionized water until its pH became neutral and then dried in an oven at 100°C for 2 hours. The synthesis process of CoFe_2O_4 -PEG was carried out with the same procedure but added with 2.346 g of PEG-4000. The adsorbents generated were characterized by using X-Ray Diffraction (Shimadzu, XD 610), SEM-EDS (JEOL-JSM 1400) and VSM (Oxford type 1.2T).

2.3 Adsorption study

The batch method was used for the adsorption study. The adsorption process is carried out by using Cr (VI) solution 50 mg/L prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ dissolving by deionized water. The adsorbents used to remove Cr (VI) were CoFe_2O_4 and CoFe_2O_4 -PEG. In this study, the adsorption process was studied by various variables, for example effect of the solution pH, contact time and the weight of the adsorbent. The effect of the solution pH was examined using Cr (VI) solution with the concentration of 50 mg/L, volume of 50 mL, weight of adsorbent of 0.1 g with the variations of pH solution at 2-9 by adding HCl and NaOH 1 M. The effect of contact time was examined in the time range of 10-200 minutes and the effect weight of adsorbent in the weight range of 0.05-0.4 g. The concentration of Cr (VI) was measured using AAS (Shimadzu AA 7000). The adsorption capacity (q_e , mg/g) of the adsorbent is calculated using to the equation:

$$q_e = \frac{(C_i - C_t)}{w} V$$

In which C_i and C_t = initial and equilibrium concentration (mg/L), V is the volume of solution (L) and W is the weight of the adsorbent (g).

To evaluate the efficiency for removal of Cr (VI) from the electroplating wastewater, adsorption experiment was conducted by 50 mL of sample, the weight of adsorbent 1.0 g, the pH and contact time using of the optimum condition have been obtained in the previous. The sorption at room temperature ($25 \pm 2^\circ\text{C}$). All measurements were made in triplicate, the final result is the average result. The electroplating wastewater has characteristic as shown in Table 1

2.1 Adsorption study

Kinetics of adsorption is used to explain the mechanism of adsorption. In this study, two kinetic models of reaction, namely pseudo first-order and pseudo-second-order were used. The equation of pseudo first-order and pseudo second-order is expressed as follows (Crittenden et al., 2005):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

In which q_e and q_t are adsorbent-phase concentration of adsorbate at equilibrium (mg-adsorbate/g-adsorbent) and adsorbent-phase concentration of adsorbate at any

Table 1. Characteristic of the electroplating wastewater

Parameters	Concentrations (mg/L)
pH	2.40
TDS	1256
COD	420
Chromium	187.6
Copper	0.86
Zink	3.56
Iron	44.6
Sulphate	6.51
Cyanide	2.45
phosphate	0.21

time (mg-adsorbate/g-adsorbent), t = time, k_1 and k_2 are the pseudo first-order (1/min) and pseudo second-order equilibrium rate constant (g/mg-min).

2.2 Isotherm of adsorption

In this study, the mathematical equations used to describe the adsorption process are the Freundlich and Langmuir isotherms. Freundlich isotherm equations are expressed as follows (Crittenden et al., 2005):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where q_e is the amount of adsorbate at an equilibrium (mg/g), K_f is Freundlich constant, $1/n$ is a heterogeneity factor and C_e is the concentration of the adsorbate at equilibrium (mg/L). The values of K_f and $1/n$ are derived from the slope and the intercept of linear equations of plot $\log q_e$ versus $\log C_e$. The linearity of the Langmuir equation is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{b_L q_0} + \frac{C_e}{q_0}$$

where q_e is the amount of adsorbate at an equilibrium (mg/g), C_e is the adsorbate concentration at an equilibrium (mg/L), q_0 and b_L are Langmuir's constant associated with adsorption capacity (mg/g) and adsorption energy (L/mg). The values of q_0 and b_L are obtained from the slope $1/q_0$ and the intercept $1/b_L q_0$ from the graph C_e/q_e versus C_e .

The important characteristic of the Langmuir isotherm equation can also be known from the R_L value (dimension factor), the value indicating the adsorption type, if $R_L > 1$, then the reaction is unfavorable. It is linear if $R_L = 1$, it is favorable if $R_L < 1$ and $R_L = 0$, which indicates an irreversible reaction. The value of R_L can be calculated using the equation:

$$R_L = \frac{1}{(1 + b_L C_0)}$$

2.3 Thermodynamics of adsorption

The temperature variations of 303, 310, 315 and 320 K were used to obtain the thermodynamic parameters of the adsorption. The thermodynamic parameters include the enthalpy value (ΔH^0), entropy (ΔS^0) and Gibbs free energy) ΔG^0 which can be calculated using the following equations (Crittenden et al., 2005):

$$\Delta G^0 = -RT \ln K_c$$

In which Where ΔG^0 is the Gibbs free energy, R is the universal gas constant (8.314 J/K mol), T is the temperature (K) and K_c is the distribution coefficient for adsorption. The value of the enthalpy and entropy can be calculated based on the slope and the intercept of the plot of $\ln K_c$ versus $1/T$ of the following equation:

$$\ln K_c = -\frac{\Delta H^0}{R} \frac{1}{T} + \frac{\Delta S^0}{R}$$

3. Results and Discussion

3.1 Characteristic of $CoFe_2O_4$ and $CoFe_2O_4$ -PEG

The phase structure of $CoFe_2O_4$ and $CoFe_2O_4$ -PEG which was measured by using XRD at 2θ range 10-80 using $K\alpha$ X-Ray source ($\lambda = 0.154$ nm) is shown in figure 1. From the figure, it can be identified that $CoFe_2O_4$ has a spinel cubic structure with the appearance of reflecting planes including (111), (311), (400), (511) and (440) (JCPDS card no 5-667). The peak of PEG does not appear because it has an amorphous structure. The addition of PEG does not change the peak position but only decreases the peak intensity. The Estimation of the particle size is calculated using the Scherrer equation as follows (Mascolo et al., 2013):

$$t = \frac{k\lambda}{L \cos \theta}$$

in which t is the size of the nanomagnetic, the Scherrer constant (0.89), λ is the wavelength of X-Ray, L is the full width at half maximum (fwhm) of the main peak and θ is Bragg angle. The size of the

CoFe₂O₄ is smaller than CoFe₂O₄-PEG, namely 20.6 and 38.7 nm, respectively.

The measurements of magnetic properties were performed using VSM at a temperature of 27°C and the magnetic field used $-10,000 \leq H \leq 10,000$ Oe. Figure 2 shows the saturation magnetization of CoFe₂O₄ and CoFe₂O₄-

PEG. These results confirm that the saturation magnetization of CoFe₂O₄ is greater than CoFe₂O₄-PEG. The saturation magnetization decreases from 22.5174 to 14.5526 emu/g. This superparamagnetic property in this study is greater than the obtained by Li *et al.*, (2014) who synthesized CoFe₂O₄-Polyvinyl chloride

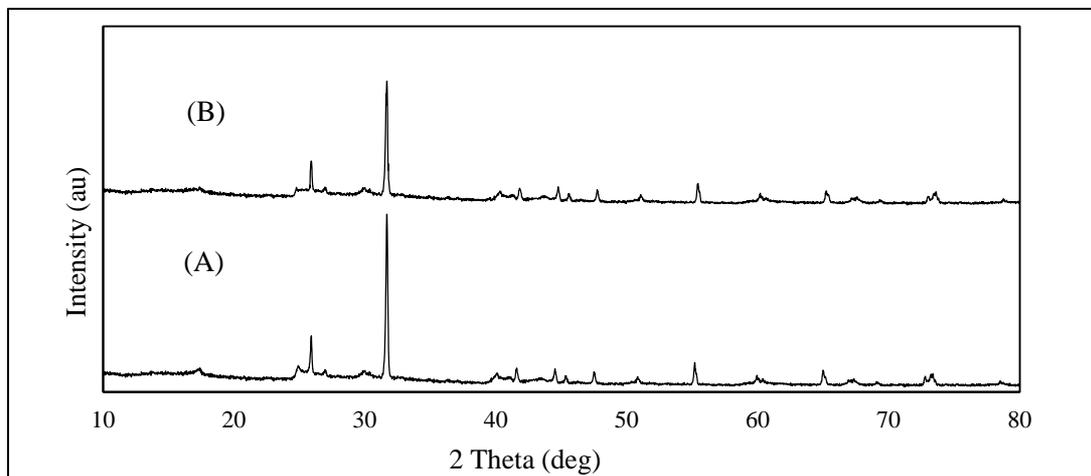


Figure 1. XRD patterns of (A) CoFe₂O₄ and (B) CoFe₂O₄-PEG

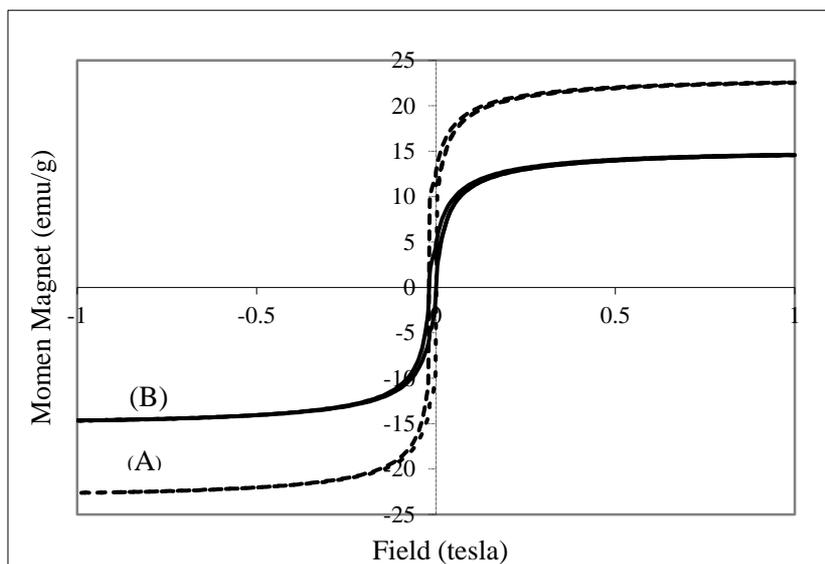


Figure 2. Magnetic Saturation of (A) CoFe₂O₄ and (B) CoFe₂O₄-PEG

obtaining magnetic saturation of 6.2183 emu/g. The magnetic properties of the adsorbent can be easily separated from the solution using an external magnet in several minutes. Figure 3 shows the morphology of CoFe_2O_4 and CoFe_2O_4 -PEG with 20,000 x magnification. The surface of CoFe_2O_4 appears to form an aggregate, after being coated with PEG,

then the surface looks more flat. The results of the elemental analysis using EDS are presented in Table 2. It can be seen that there is a decrease in Fe, O and Co elements after the occurrence of coating with PEG. The emergence of C element indicates that the coating process has been successful.

Table 2. Element composition of CoFe_2O_4 and CoFe_2O_4 -PEG

Element	Percentage (%)	
	CoFe_2O_4	CoFe_2O_4 -PEG
Fe	39.63	31.90
O	48.75	36.22
Co	11.62	8.25
C	-	23.63

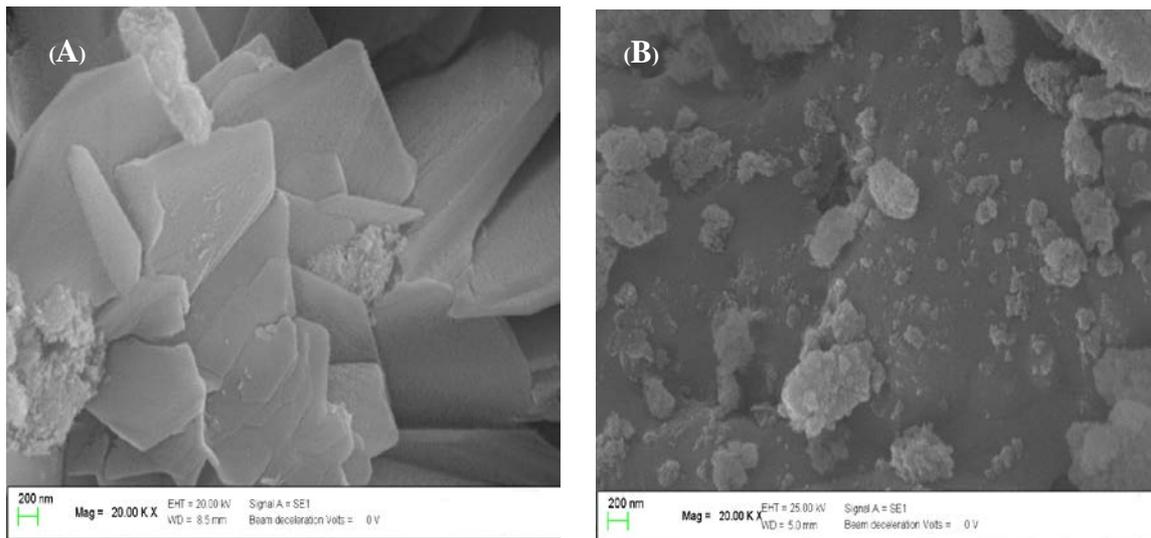


Figure 3. Morphology of (A) CoFe_2O_4 and (B) CoFe_2O_4 -PEG

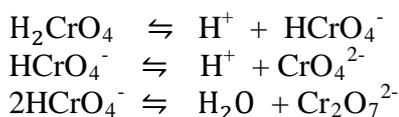
3.2 Adsorption of Cr (VI) by CoFe_2O_4 and CoFe_2O_4 -PEG

Effect of Solution pH

The pH of the solution affects adsorption process between the heavy metal ions and the adsorbents. The protonation process and the deprotonation of the adsorbent are affected by the pH of the solution. Figures 4 show the effect of pH on the adsorption of Cr (VI) by CoFe_2O_4 and CoFe_2O_4 -PEG. In this study, the effect of pH on the adsorption capacity of Cr (VI) was examined in the range of 2-9 with ion concentration of Cr (VI) of 50 mg/L, volume of 50 mL, weight of adsorbent 0.1 g.

At acid solution, there is a mutual electrostatic attraction between Cr (VI) which dominant form is HCrO_4^- , has a negatively charged with a positively charged adsorbent, so that the adsorption capacity is large. Another study showed that pHpzc of CoFe_2O_4 is 7.4 (Ghaemi et al., 2014). At pH below pHpzc , the

adsorbents are positively charged resulting mutual attraction with Cr (VI) being negatively charged. In this study, the pH value of 3 was the optimum adsorption using CoFe_2O_4 and CoFe_2O_4 -PEG adsorbents. The optimum adsorption process was obtained at a low pH due to the free energy of the HCrO_4^- ion which has one charge, which is lower than that of the CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ion having 2 charges. The ion equilibrium reaction of Cr (VI) is as follows (Gurgel et al., 2009):



The increase in pH leads to an increase of OH^- ions in the solution, resulting in the competition between Cr (VI) in the form is CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ and OH^- ions bound on the adsorbent so that the adsorption capacity decreases (Kumar and Jena, 2017; Mallick et al., 2006; Zhang et al., 2012).

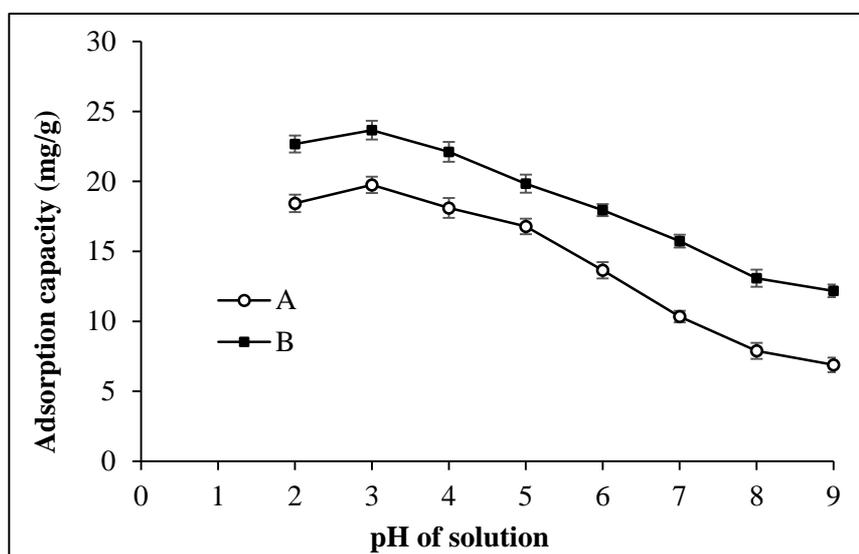


Figure 4. Effect of pH on the adsorption capacity of (A) CoFe_2O_4 and (B) CoFe_2O_4 -PEG with initial concentration Cr (VI) of 50 mg/L, volume of 50 mL, weight of adsorbent 0.1 g and contact time of 20 min.

Effects of Contact Time

The effects of contact time on Cr (VI) adsorption process using CoFe_2O_4 and CoFe_2O_4 -PEG adsorbents are shown in Figure 5. In the figure, it appears that the adsorption process initially fast, then slows down until it reaches an equilibrium. After reaching the equilibrium, there is no significant change in adsorption capacity. In this study, the adsorption equilibrium time using CoFe_2O_4 and CoFe_2O_4 -PEG was obtained at the same time, namely 35 minutes with the adsorption capacity respectively of 20.67 and 24.45 mg/g. The adsorption equilibrium time obtained in this study was faster than Cr (VI) adsorption using nanomagnetic of Fe_3O_4 at 60 minutes (Ciftci and Ersoy, 2016).

Effect Adsorbent Weight

Figures 6 show the changes in adsorption capacity of CoFe_2O_4 and CoFe_2O_4 -PEG toward Cr (VI) in the adsorbent weight range from 0.05 to 0.4 g. The adsorption process was carried out at pH 3, the Cr (VI) concentration of 50 mg/L, the volume of 50 mL and the contact time of 35 minutes. On the figure it can be seen that in the first stage, the adsorption capacity increases, because the addition of adsorbent causes the increase the number of active sites of the adsorbent. Furthermore, with an addition of more than 0.1 g, there is a decrease in adsorption capacity. This occurs because the amount of Cr (VI) in solution is fixed while the number of active sites increases so that not enough Cr (VI) to occupy in the active sites.

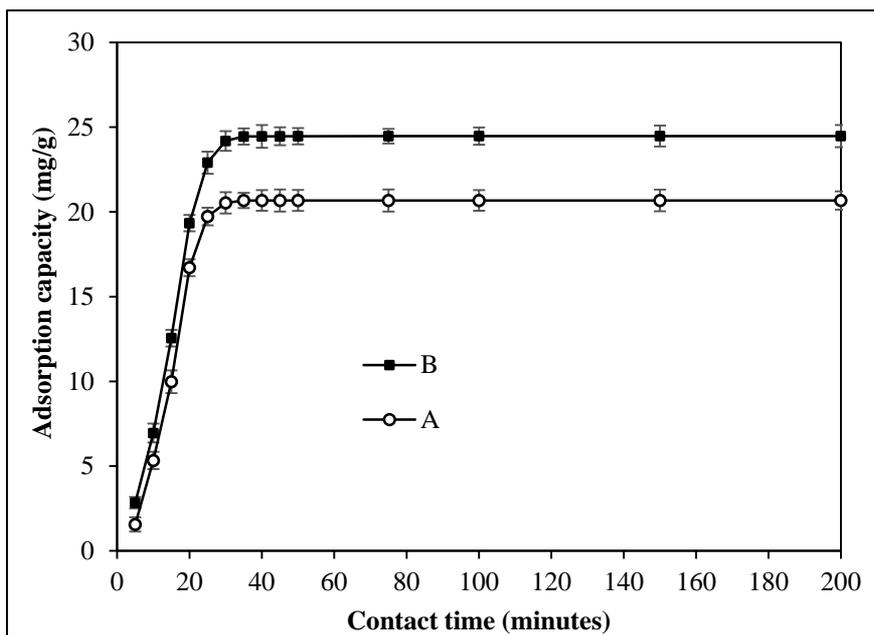
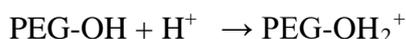


Figure 5. Effect of contact time on the adsorption capacity of (A) CoFe_2O_4 and (B) CoFe_2O_4 -PEG with initial concentration Cr (VI) of 50 mg/L, volume of 50 mL, weight of adsorbent 0.1 g and pH of 3.

The adsorption capacity of CoFe_2O_4 -PEG to Cr (VI) is greater than CoFe_2O_4 -PEG which is an organic polymer with the formula $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, in the acid condition which is positively charged in accordance with the reaction:



Positively charged PEG may attract negatively charged Cr (VI), thus increasing adsorption capacity of the adsorbents.

3.3 Kinetics of adsorption

Kinetics adsorption is one of the important parameters in the adsorption process. The kinetics adsorption is needed to know the mechanism of the adsorption process (Gebru and Das, 2017). To find out whether a reaction is in accordance with pseudo first-order or pseudo second-order can be done by looking at the value

of the coefficient of determination (R^2). The kinetic parameters using Cr (VI) 50 mg/L solution, volume of 50 mL, solution pH of 3 and weight of adsorbent 0.1 g are presented in Table 3.

The result of the study shows that the value of R^2 on pseudo second-order kinetic model is bigger than that of the pseudo first-order. Thus, the pseudo second-order kinetics model is more suitable for describing the kinetic model using both CoFe_2O_4 and CoFe_2O_4 -PEG adsorbents. The pseudo second-order performed that the adsorption process dependent on the amount of adsorbate and active sites on the surface of the adsorbents. Also, the reaction rate is chemically controlled (Vibhatabandhu and Srithongouthai, 2017). The same results were obtained on Cr (VI) adsorption with micro silica composite and paper mill sludge (Zhang *et al.*, 2012; Gorzin and Abadi, 2017).

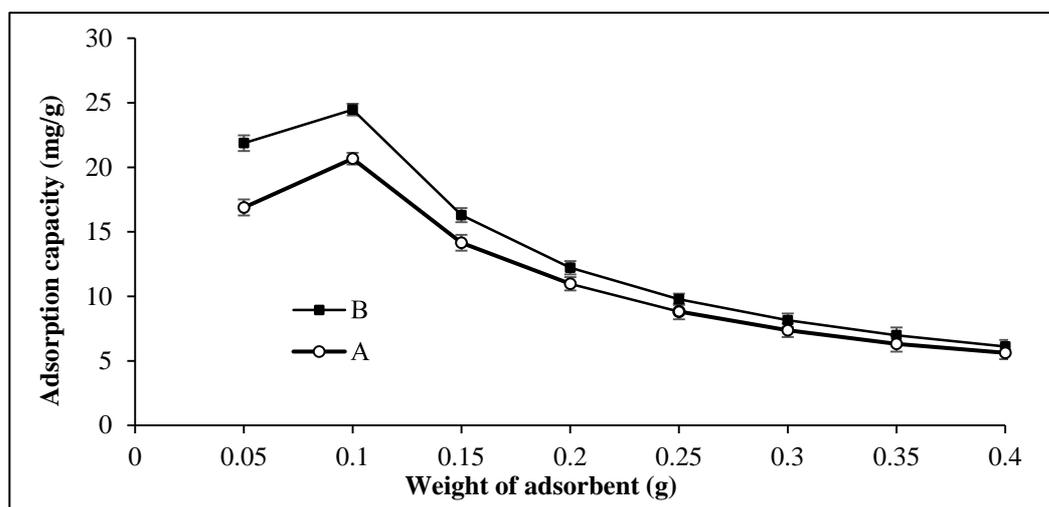


Figure 6. Effect weight of adsorbent on the adsorption capacity of (A) CoFe_2O_4 and (B) CoFe_2O_4 -PEG with initial concentration Cr (VI) of 50 mg/L, volume of 50 mL, contact time of 35 min and pH of 3.

Table 3. Kinetic adsorption parameters

Parameters	CoFe ₂ O ₄		CoFe ₂ O ₄ -PEG	
	Pseudo first-order	Pseudo second-order	Pseudo first-order	Pseudo second-order
R ²	0.8914	0.9952	0.9733	0.9973
k ₁ (1/min)	0.1941	-	0.1837	-
k ₂ (g/mg·min)	-	0.0036	-	0.0023
q _e (mg/g)	84.681	26.445	102.837	22.624
q _{eksp} (mg/g)	20.670		24.450	

Table 4. Isotherm parameters for adsorption of Cr (VI) onto CoFe₂O₄ and CoFe₂O₄-

Isotherm	Parameters	Value	
		CoFe ₂ O ₄	CoFe ₂ O ₄ -PEG
Freundlich	R ²	0.9687	0.9625
	K _f	12.990	9.310
	1/n	0.4896	0.3958
Langmuir	R ²	0.9909	0.9959
	q ₀	40.983	42.107
	b _L	0.249	0.250
	R _L	0.0393	0.0385

PEG

Isotherm of Adsorption

The adsorption isotherm shows the relationship between the amount of the adsorbed substance and the concentration of the substance in the equilibrium at a fixed temperature. Freundlich isotherm is used for the adsorption process in which the adsorbent surface heterogeneity and adsorption heat occur (Kardar *et al.*, 2016; Dong *et al.*, 2014). The Langmuir isotherm equation illustrates that the adsorbate molecule has the same energy adsorbed on the adsorbent, this process is the monolayer adsorption (Kardar *et al.*, 2016). Figures 7 show that the adsorption of Cr (VI) using CoFe₂O₄ and CoFe₂O₄-PEG using the Langmuir equation has the

linearity of R², respectively of 0.9909 and 0.9959. The value of R² is greater than that using the Freundlich equation of 0.9687 and 0.9625. Table 4 shows the adsorption isotherm parameters of Cr (VI) in CoFe₂O₄ and CoFe₂O₄-PEG.

The value of 1/n < 1 indicates that the surface of the adsorbent is homogeneous (Hashim *et al.*, 2011). In this study, the value of 1/n using an adsorbent of CoFe₂O₄ is 0.4896, while that of CoFe₂O₄-PEG is 0.3958. Other parameters are R_L values of 0.0393 and 0.0385. The adsorption process is favourable if R_L < 1. It is clear that the Langmuir isotherm is more suitable for describing the adsorption reaction of Cr

(VI) in CoFe_2O_4 and CoFe_2O_4 -PEG. The maximum adsorption capacity of CoFe_2O_4

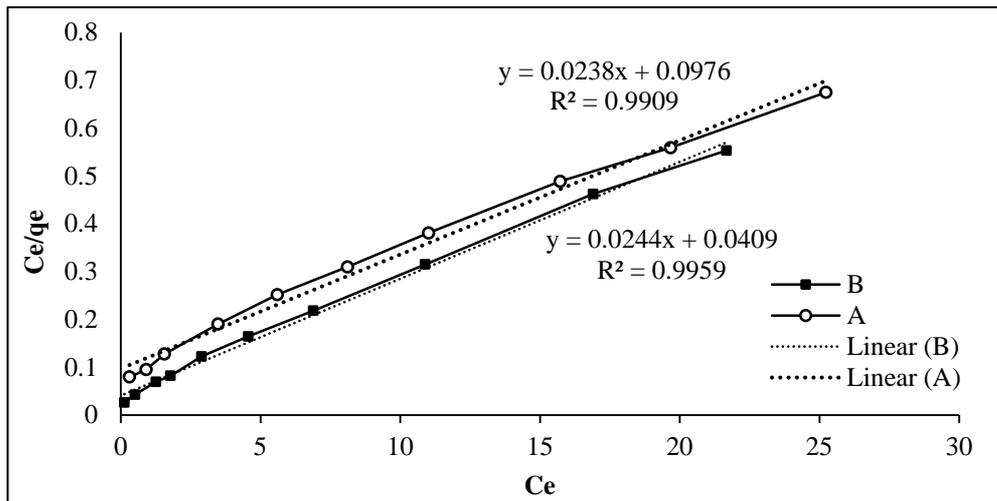


Figure 7. Adsorption Isotherm of (A) CoFe_2O_4 and (B) CoFe_2O_4 -PEG

Table 5. Maximum adsorption capacity of some adsorbents for removal of Cr (VI)

Adsorbents	Adsorption capacity (mg/g)	References
Activated carbon	3.46	Selvi et al., 2000
MnFe_2O_4	31.5	Hu et al., 2005
Organobentonit	5.12	Ramos et al., 2008
Fe_3O_4	41	Amin et al., 2010
Carbon mikro silika composite	18.9	Zhang, 2012
Activated carbon	7.8	Rai et al., 2016
Red mud Modified Lanthanum	17.35	Cui et al., 2016
Paper mill sludge	23.18	Gorzin and Abadi, 2017
CoFe_2O_4	40.983	In this study
CoFe_2O_4 -PEG	42.107	In this study

and CoFe_2O_4 -PEG was obtained at 40.983 and 42.107 mg/g, respectively. Table 5 shows maximum adsorption capacity of Cr (VI) some adsorbent. Compared the other

adsorbents, CoFe_2O_4 and CoFe_2O_4 -PEG have a higher adsorption capacity.

3.4 Thermodynamic parameters

The spontaneity of the reaction can be disclosed on the basis of thermodynamic parameters. The value of the thermodynamic parameter can be used as an indicator in its application. The values of free energy change, enthalpy and entropy are presented in Table 6. The change in free energy has a negative value, indicating that the reaction occurs spontaneously. The higher the temperature, the more negative the free energy value. This means that the adsorption process increases with increase temperature. The enthalpy change has a positive value, indicating that the reaction is endothermic, while the entropy change has a negative value, showing no significant occurrence in the internal structure of the adsorbent.

3.5. Adsorption of Cr (VI) from the electroplating wastewater

The adsorption process of Cr by both adsorbents, namely CoFe_2O_4 and $\text{CoFe}_2\text{O}_4\text{-PEG}$ was carried out by using batch method at 35 minutes contact time at room temperature, the volume of 50 mL, the pH of the waste was conditioned at pH 3, and the added adsorbent weight

was 1.0 g. The efficiency for removal of Cr (VI) using CoFe_2O_4 and $\text{CoFe}_2\text{O}_4\text{-PEG}$ are shown in Table 7.

In the wastewater of the electroplating industry contains many cations and anions such as Cr, Cu, Zn, Fe, sulphate, cyanide, and phosphate. It causes competitions among the ions to be adsorbed by the adsorbents. The adsorption efficiency of Cr (VI) using $\text{CoFe}_2\text{O}_4\text{-PEG}$ adsorbent is greater than CoFe_2O_4 . PEG also contributes to binding with Cr (VI) thereby increasing the efficiency of removal Cr (VI).

4. Conclusions

In this study, CoFe_2O_4 and $\text{CoFe}_2\text{O}_4\text{-PEG}$ have been successfully synthesized by co-precipitation method, then both adsorbents are used to removal Cr (VI). The adsorbent of CoFe_2O_4 and $\text{CoFe}_2\text{O}_4\text{-PEG}$ are magnetic properties so that after the adsorption process, they can be separated from the solution quickly using a permanent magnet. The coating with PEG causes reduced magnetic properties but increased adsorption capacity. The adsorption process of Cr (VI) using both

Table 6. Thermodynamic parameters

Adsorbents	Temp.(K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)
CoFe_2O_4	303	-2.737	21.342	-79.459
	310	-3.291		
	315	-3.669		
	320	-4.096		
$\text{CoFe}_2\text{O}_4\text{-PEG}$	303	-3.205	20.661	-79.220
	310	-4.077		
	315	-4.321		
	320	-4.594		

Table 7. The Efficiency for removal of Cr (VI) from electroplating industry wastewater

Adsorbents	Before treatment (mg/L)	After treatment (mg/L)	Efficiency (%)
CoFe ₂ O ₄	186.94 ± 1.55	58.92 ± 1.12	68.48 ± 0.45
CoFe ₂ O ₄ -PEG	186.94 ± 1.55	49.73 ± 0.89	73.39 ± 0.67

adsorbents have the same mechanism, follows Langmuir isotherms and kinetics reaction in accordance with the pseudo second-order. The result of this study showed that CoFe₂O₄-PEG has the efficiency for removal of Cr (VI) from electroplating wastewater is greater compared CoFe₂O₄. The CoFe₂O₄-PEG has potential to applicable for electroplating wastewater, the adsorbent as fast sorption, its separation fast, not filtered so low cost.

Acknowledgements

The authors would like to gratefully acknowledge to Sriwijaya University, Palembang, Indonesia for funding research from the “Unggulan Kompetitif” research grant of Sriwijaya University No.042.01.2.400953/2017.

References

Alswat AA, Ahmad MB, Saleh TA. Zeolite modified with copper oxide and iron oxide for lead and arsenic adsorption from aqueous solutions. *Journal of Water Supply Research and Technology* 2014; 65(4): 465-79.

Amin MM, Khodabakhshi, Mozafari M, Bina B, Kheiri S. Removal of Cr (VI) from simulated

electroplating wastewater by magnetite nanoparticles. *Environmental Engineering and Management Journal* 2010; 9(7): 921-27.

- Bishnoi NR, Bajaj M, Sharma N. Adsorption of Cr (VI) from aqueous and electroplating wastewater. *Environmental Technology* 2007; 25: 889-905.
- Ciftci H, Ersoy B. 2016. Adsorption of Cr (VI) ions on magnetite nano-particles (Fe₃O₄) kinetic and thermodynamic studies. *El-Cezeri Journal of Science and Engineering* 2016; 3(3): 417-27.
- Crittenden JC, Trussell RR, Hand DW, Howe KJ, Tchobanoglous G. *Water treatment: Principles and Design*. 2nd. John Wiley and Sons Inc. New Jersey, U.S. 2005; 266-68.
- Cui YW, Li J, Du ZF, Peng YZ. Cr (VI) adsorption on red mud modified by lanthanum: performance, kinetics, and mechanisms. *Plos One* 2016; ed September 22: 1-16.
- Dong L, Zhu Z, Qiu Y, Zhao J. Removal of lead from aqueous solution by hydroxyapatite/manganese dioxide composite. *Frontiers of Environmental Science & Engineering* 2016; 10(1): 28-36.
- Fang X, Zhang G, Chen J, Wang D, Yang F. Electrochemical reduction of hexavalent chromium on two step electro synthesized one dimensional polyaniline nanowire. *International Journal Electrochemical Science* 2012; 7: 11847-58.
- Farooq U, Kozinski JA, Khan, MA, Athar, M. Biosorption of heavy metal ions using wheat based biosorbents- a review of the recent

- literature. *Bioresource Technology* 2010; 101: 5043-53.
- Foroughi F, Tabrizi SAH, Amighian J, Teluri AS. A designed magnetic CoFe_2O_4 -hydroxyapatite core-shell nanocomposite for Zn (II) removal with high efficiency. *Ceramics International* 2015; 41: 6844-50.
- Gebru KA, Das C. Removal of Pb(II) and Cu (II) ions from wastewater using composite electrospun cellulose acetate/titanium oxide (TiO_2) adsorbent. *Journal of Water Process Engineering* 2017; 16: 1-13.
- Ghaemi M, Absalan G, Sheikhan L. Adsorption characteristics of titan yellow and congo red on CoFe_2O_4 magnetic nanoparticles. *Journal of Iranian Chemical Society*. 2014; 11(6): 1759-66
- Gorzin F, Abadi MMBR. Adsorption of Cr (VI) from aqueous solution by adsorbent prepared from paper mill sludge: kinetics and thermodynamics studies. *Adsorption Science and Technology* 2017; 0(0): 1-21.
- Gurgel LVA, De Melo JCP, De Lena JC, Gil LF. Adsorption of chromium (VI) ion from aqueous solution by succinylated mercerized cellulose functionalized with quaternary ammonium groups. *Bioresource Technology* 2009; 100: 3214-20.
- Hashim MA, Mukhopadhyay S, Sahu JN, Sengupta B. Remediation technologies for heavy metal contaminated groundwater. *Journal of Environmental Management* 2011; 92: 2355-88.
- Hu J, Lo IMC, Chen G. Fast removal and recovery of Cr (VI) using surface-modified jacobsite (MnFe_2O_4) nanoparticles. *Langmuir* 2005; 21: 11173-79.
- Ilanakoon N. Use of iron oxide magnetic nanosorbents for Cr (VI) removal from aqueous solution: A review. *Journal of Engineering Research and Applications* 2014; 4(10): 55-63.
- Kakavandi B, Jafari AJ, Kalantary RR, Nasser S, Ameri A, Esrafiy A. Synthesis and properties of Fe_3O_4 -activated carbon magnetic nanoparticles for removal of aniline from aqueous solution: equilibrium, kinetic and thermodynamic studies. *Iranian Journal of Environmental Health Science and Engineering* 2013; 10(19): 1-9.
- Kardar ZS, Beyki MH, Shemirani F. Takovite aluminosilicate@ MnFe_2O_4 nanocomposite, a novel magnetic adsorbent for efficient preconcentration of lead ions in food samples. *Food Chemistry* 2016; 209: 241-47.
- Kim DH, Nikles DE, Brazel CS. Synthesis and characterization of multifunctional chitosan- MnFe_2O_4 nanoparticles for magnetic hyperthermia and drug delivery. *Materials* 2010; 3: 4051-65.
- Kotas J, Stasicka Z. Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution* 2000; 107: 263-83.
- Kumar A, Jena HM. Adsorption of Cr (VI) from aqueous solution by prepared high surface area activated carbon from fox nutshell by chemical activation with H_3PO_4 . *Journal Environmental Chemical Engineering* 2017; 5(2): 1826-42.
- Li Z, Gondal MA, Yamani ZH. Preparation of magnetic separable CoFe_2O_4 /PAC composite and adsorption of bisphenol A from aqueous solution. *Journal of Saudi Chemical Society* 2014; 18: 208-13.
- Mallick S, Dash S.S, Parida K.M. Adsorption of hexavalent chromium on manganese nodule leached residue obtained from NH_3 - SO_2 leaching. *Journal of Colloid and Interface Science* 2006; 297: 419-25.
- Mascolo MC, Pei M, Ring TA. Room temperature co-precipitation synthesis of magnetite nanoparticles in a large pH window with different bases. *Materials* 2013; 6: 5549-67.
- Mc Guire, MJ, Blute NK, Qin G. Hexavalent chromium removal using anion exchange and reduction with coagulation and filtration. Awwa RF, Glendale and USEPA, USA. 2007; 2-18.
- Mohamed A, Nasser Ws, Osman TA, Toprak MS, Muhammed M, Uheida A. Removal of chromium (VI) from aqueous solutions using surface modified composite nanofibers. *Journal of Colloid and Interface Science* 2017; 505: 682-91.
- Pang Y, Zeng G, Tang L, Zhang Y, Liu Y, Lei X, Li Z, Zhang J, Liu Z, Xiong Y. Preparation

- and application of stability enhanced magnetic nanoparticles for rapid removal of Cr (VI). *Chemical Engineering Journal* 2011; 174: 222-27.
- Rai MK, Shahi G, Meena V, Meena R, Chakraborty S, Singh RS, Rai, BN. Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated carbon activated H_3PO_4 . *Resource Efficient Technologies* 2016; 2: 63-70.
- Ramakrishnariah CR, Prathima B. Hexavalent chromium removal from industrial wastewater by chemical precipitation method. *International Journal of Engineering Research and Applications* 2012; 2(2): 599-603.
- Ranjeh G, Radmanesh M, Kiafar A. Nanosized $NiFe_2O_4$ /active carbon composites as adsorbent for dyes and colours. *Science Journal of Chemistry* 2015; 3(2): 28-34.
- Ramos RL, Azuara AJ, Flores PED, Corronado RMG, Barron JM, Mendoza MS. Adsorption of chromium (VI) from aqueous solution on a surfactant modified zeolite. *Colloids and Surfaces A: Physicochemical Engineering Aspects* 2008; 230: 35-41.
- Santhosh CS, Kollu P, Felix S, Velmurugan V, Jeong SK, Grace AN. $CoFe_2O_4$ and $NiFe_2O_4$ @graphene adsorbents for heavy metal ions - kinetics and thermodynamic analysis. *Royal Society of Chemistry* 2015; 5: 28965-72.