Effectiveness of polyethylene glycol-coated silica on ions adsorption in industrial wastewater

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Effectiveness of polyethylene glycol-coated silica on ions adsorption in industrial wastewater

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Abstract: The effect of coating silica with polyethylene glycol on the adsorption of iron and phosphate ions in industrial wastewater was investigated. Variable factors were temperature and time of coating, PEG concentration, and PEG to silica ratio. Infrared spectroscopy and scanning electron microscopy were used to evaluate the chemical structure and morphology of PEG-coated silica. Optimum iron and phosphate ions removal efficiency was obtained using a coating temperature of 50°C, a coating time of 15 min, a PEG concentration of 20%, and a PEG to silica ratio of 1:3.

Keywords: adsorption, silica, PEG, coating.

Wpływ powlekania krzemionki glikolem polietylenowym na adsorpcję jonów ze ścieków przemysłowych

Abstrakt: Zbadano wpływ powlekania krzemionki glikolem polietylenowym na adsorpcję jonów żelaza i fosforanów ze ścieków przemysłowych. Czynnikami zmiennymi były temperatura i czas powlekania, stężenie PEG oraz stosunek PEG do krzemionki. Do oceny budowy chemicznej i struktury krzemionki powlekanej PEG stosowano spektroskopię w podczerwieni i skaningową mikroskopię elektronową. Optymalną skuteczność usuwania jonów żelaza i fosforanów uzyskano stosując temperaturę powlekania 50°C, czas powlekania 15 minut, stężenie PEG 20% oraz stosunek PEG do krzemionki 1:3.

Słowa kluczowe: adsorpcja, krzemionka, PEG, powlekanie.

In the last few years, the manufacture of value-added products in Indonesia has been increasing rapidly. The development of this industry significantly contributes to environmental pollution, including water pollution [1]. Industrial growth is accelerating in Indonesia, which may affect the quality of the ecosystem, especially water, from incomplete disposal of liquid waste from industry. Data collected by Indonesia's Bureau of Environmental Statistics confirms that water pollution levels in Indonesia have increased by 10% in recent years [2].

There are ways to assess water and wastewater quality, either by on-site or laboratory-based measurement. The parameters that can be detected directly on-site are pH, total dissolved solids (TDS), and electrical conductivity (EC). Meanwhile, parameters that required to be checked in the laboratory are chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), total hardness, alkalinity, color, residual chlorine (Cl_2), and turbidity [3]. Wastewater also commonly contains iron (Fe), which can negatively impact the environment. Iron ions caused

toxicity and regeneration of planarians, as proved in [4]. Iron concentration in wastewater may indicate the presence of pathogens or other contaminants which can cause adverse health effects for the human body [5]. The vital parameter which should be considered in wastewater is phosphate concentration. This ion can cause eutrophication in water and aquatic ecosystems, and if this ion is exposed to humans, it will impact serious health risks [6].

Adsorption is a promising method for preventing water pollution caused by industrial waste in Indonesia. Silica has been widely used as an iron ion adsorbent in wastewater. The application of silica is based on its properties, which include a distinct surface area and large pores. Several studies have been conducted to obtain silica as a heavy metal adsorbent with reasonable efficiencies, such as absorbing heavy metals from wastewater, resulting in an iron reduction by more than 0.1 ppm [7]. Silica also has been widely used as an adsorbent to reduce several pollutants in water and wastewater treatment, such as Pb^{2+} [8], Mn^{2+} [9], Cd [10]. SG should be modified. The SG was modified with D-glycine (Si-Gly, Mg^{2+} [11] Cu^{2+} [12], and NO_3^- [7].

Silica, with the chemical formula SiO_2, is an oxide compound with no active group. Several studies report silica-based optimization for heavy metal adsorption, such as using sulfonate functional groups [11]. The perfor-

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mance of silica as metal adsorbent has been proved by [13], which used silica as Cu adsorbent, and was reported effective. Previous studies have also focused on maximizing silica's potential combined with polymers, particularly polyethylene glycol (PEG), such as by physical and chemical coating [14].

PEG has an oxyethylene-containing polyether chain as a polymer with a main hydroxyl group at the end. With the help of intermolecular interactions, it can create a double helix. PEG functional groups can also provide hydrogen bonding and dipole-dipole interactions [15].

This study aims to increase the effectiveness of silica by using a coating method with PEG. FTIR and SEM methods were used to determine the chemical structure and morphology of PEG-coated silica. The absorption ability of PEG-coated silica will be evaluated as an adsorbent for the absorption of iron (Fe) and phosphate (PO_4^{3-}) ions in wastewater. The influence of PEG concentration, PEG-silica ratio, coating time, and coating temperature on removing those ions was investigated.

EXPERIMENTAL PART

Materials

The materials used in this study were commercial silica gel, PEG 4000 (Sigma Aldrich), ethanol (Merck), KH_2PO_4 (Merck), ammonium molybdate (Sigma Aldrich), $SnCl_2$ (Merck), H_2SO_4 (Merck), glycerol 85% (Merck), and distilled water.

Methods

Preparation of PEG-coated silica

Silica was added to PEG dissolved in ethanol and mixed for 15 min. Then silica was separated from the PEG solution, dried and stored in a desiccator for 24 h. PEG solutions with a concentration of 5, 10, 15 and 20% were used, the coating time was 10, 20, 30 or 40 min, the coating temperature was 30, 40, 50 or 60°C, and the ratio of PEG to silica was 1:1, 1:2 , 1:3 or 1:4.

Characterization of PEG-coated silica

Identification of the functional group in the PEG-coated silica was conducted using Fourier Transform Infra-Red (FTIR) Spectrum 400 Series Perkin Elmer. Scanning electron microscope (SEM) (Hitachi SU3500, Tokyo, Japan) instruments were used to investigate the morphology of PEG-coated silica. Elemental analysis of the PEG-coated silica was carried out by using MT-6 CHN Corder (Yanaco, Kyoto, Japan).

Adsorption of anion and cation procedures

Synthetic phosphate wastewater (KH_2PO_4) was used to evaluate the effectiveness of PEG-coated silica as adsor-

bent of phosphate ions in this study. As mother liquor, 1000 ppm of KH_2PO_4 was diluted with distilled water using the dilution formula until the concentration of the final solution reached 20 ppm. A volume of 25 mL solution was put into a beaker glass. Subsequently, 0.25 mL of ammonium molybdate and one drop of $SnCl_2$ were added. Then the solution was stirred and allowed to react for 5 minutes. For the application of wastewater treatment, PEG-coated silica was contacted with wastewater sample and then stirred with a rotation speed of 250 rpm. After being contacted for 15 minutes, the wastewater sample was filtered and put into the cuvette for measurement using Spectrophotometry UV-Vis. For the adsorption of iron ions, the $FeCl_3$ solution of 20 ppm was used as targeted wastewater. The procedure of adsorption followed the adsorption process of phosphate ions. The measurement of phosphate concentration was conducted using Spectrophotometry UV-Vis Thermo Scientific Genesys 10S at a wavelength of 450 nm. While the concentration of iron ions was measured using atomic absorption spectrophotometer (AAS) Shimadzu AA-6800.

RESULTS AND DISCUSSION

Synthesis and characterization of PEG-coated silica

The ether oxygen atoms of PEG (-δO-CH_2-CH_2-) have a high affinity for Si–OH silanol groups. Therefore, it plays the role of proton acceptors in the hydrogen bonding between PEG macromolecules and primary silica particles [16]. Based on [17], cure times can be shortened and increase productivity by covering silanol groups on the silica surface using PEG.

PEG-coated silica was characterized using Fourier transform infra-red spectroscopy (FTIR) to determine and confirm the bonding modes of the formed organic compound groups. FTIR characterization was performed using the mid-infrared wavelength range from 4000 to 400 cm⁻¹ as shown in Fig. 1. A characteristic peak for PEG-
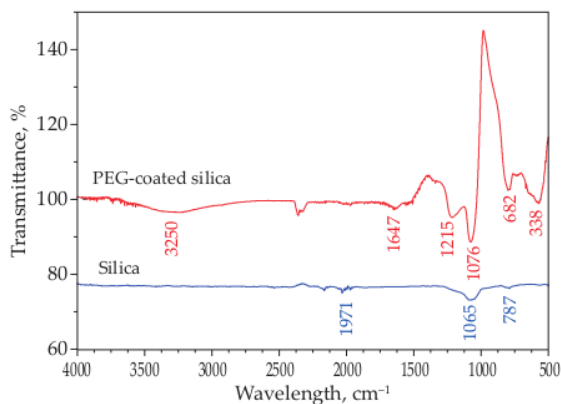

Fig. 1. FTIR spectra of PEG-coated silica

T a b l e 1. IR spectrum wavelengths of PEG-coated silica

Bond type	PEG-coated silica	Pure silica	Reference [18]
	Wavelength, cm^{-1}		
OH *stretching*	3250	1971	3000–3700
	1647		1650–1900
C–O *stretching*	1215	–	1500–800
Si–O–Si *asymmetrical stretching*	1076; 682; 337	1065; 786	1130–800

coated silica appeared to be presented between 3000 and 3700 cm^{-1}. In particular, the broad peaks at 3250 cm^{-1} and 1647 cm^{-1} were assigned to the –OH stretching vibrations of PEG-coated silica resulted in this study [18].

The bonding of silica and PEG is due to dipole-dipole interactions. The ions between the long-chain oxygen atoms of PEG and silica were coordinated to form a double helix. Therefore, it functions as an ion-exchange active site at a wavelength of 3250 cm^{-1} and is identified as an alcohol group (–OH). Hence, the wavelength of 1647 cm^{-1} was determined as the –OH group attached to silica. Silica was detected as silica gel at 682 cm^{-1}, while in pure silica, it represented at a wavelength of 786 cm^{-1}. In PEG-coated silica, strong bands at 1076 cm^{-1} and 337 cm^{-1} are associated with asymmetric Si-O-Si stretch bonds. As for pure silica, the associated wavelength of this bond is identified at 1065 cm^{-1}. Additionally, the wavelength of 1215 cm^{-1} was also detected as a C–O bond of PEG. However, this bond is not detected in pure silica. The specific functional groups which displayed spectrum from Fig. 1 are shown in Table 1.

The morphology surface of PEG-coated silica was investigated using SEM as presented in Fig. 2. There were only slight differences in the surface morphology of the commercial silica gel and the PEG-coated silica. This is because the reaction between PEG and silica gel is just a physical coating.

The PEG-coated silica was characterized by elemental analysis to obtain information on the percentage of carbon and hydrogen. No carbon was found in the silica gel and the hydrogen content was 0.68%. The carbon and hydrogen content of the PEG-coated silica was 0.34% and 0.63%, respectively.

Adsorption of anion and cation in the wastewater

The effectiveness of the adsorbent is affected by coating time, PEG to silica ratio, PEG concentration, and coating temperature. Thus, the adsorption performance of PEG-coated silica was observed for various conditions: concentration of PEG (5; 10; 15; 20%), coating time (10; 20; 30; 40 min), coating temperature (30; 40; 50; 60°C), and the ratio of PEG to silica (1:1; 1:2; 1:3; 1:4). The silica surface consists of hydrogen atoms which bonded tetrahedral with silica atoms and hydroxyl groups. These hydroxyl groups and Si-O-Si have an essential role in iron adsorption [19].
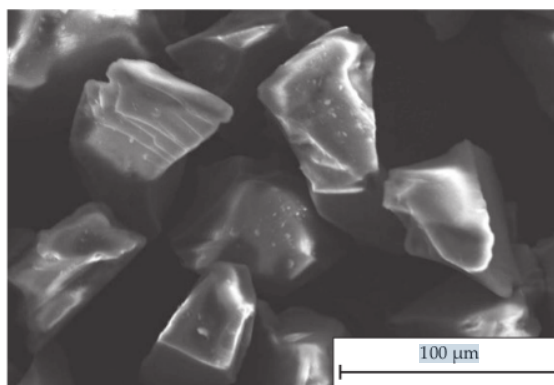
Effect of coating time

Effect of coating time on phosphate and iron adsorption wastewater is shown in Fig. 3. It can be concluded that the longer the contact time, the higher the adsorption of Fe cations and PO$_4^{3-}$ anions. This shows that the longer the coating time, the more ions are absorbed into the surface pores. The optimal time for coating time occurs at 30 minutes, but at 40 minutes there is a decrease in the adsorption of Fe and PO$_4^{3-}$. This is because all active sites

a)
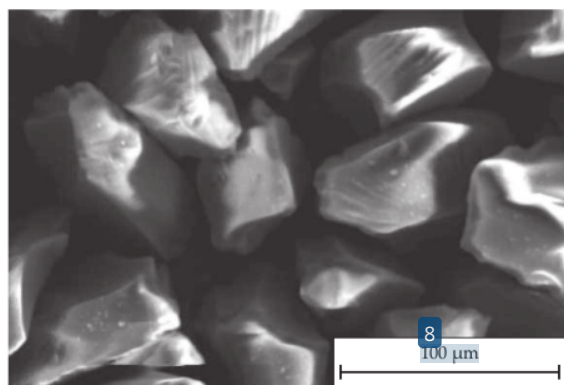
b)

Fig. 2. SEM images of silica-gel (a), and PEG-coated silica (b)
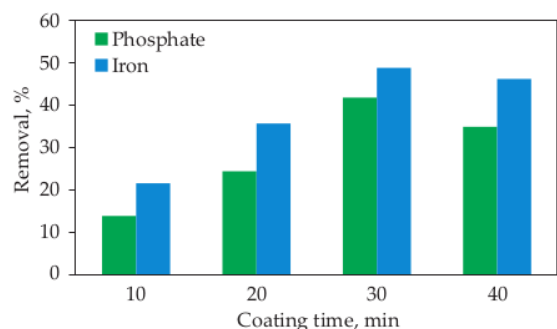
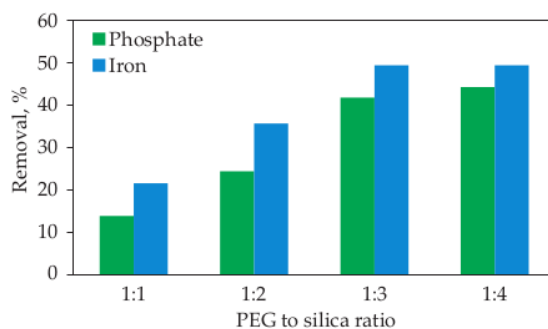Fig. 3. Effect of coating time on iron and phosphate adsorption in wastewater

Fig. 4. Effect of PEG-Silica ratio on iron and phosphate adsorption in wastewater
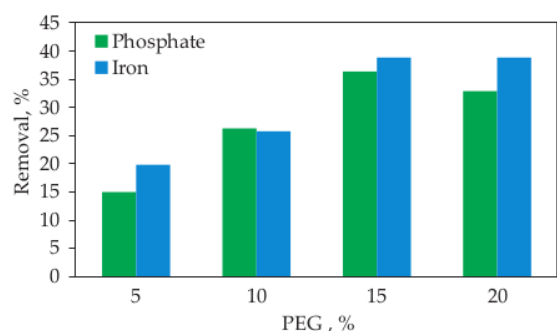

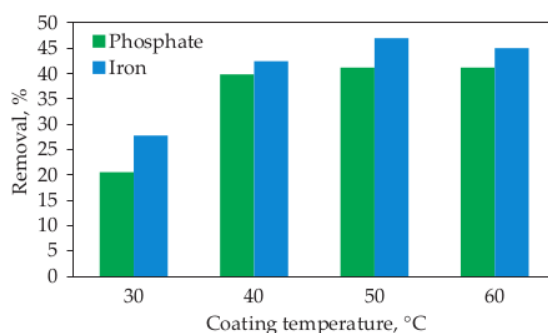Fig. 5. Effects of PEG concentration in iron and phosphate adsorption

Fig. 6. Effect of coating temperature in iron and phosphate adsorption

are occupied with Fe and PO_4^{3-}, reducing the adsorption ability [20] it is necessary to remove heavy metals in contaminated water to eliminate the associated risks. This study focused on the removal of heavy metal ions using silica sulfuric acid (SSA).

PEG-silica ratio

Fig. 4 shows the performance of PEG-coated silica in various PEG to silica ratio. The optimum ratio of PEG to silica for Fe and PO_4^{3-} adsorption is 1:3. Higher PEG-silica ratio increases the effectiveness of Fe and PO_4^{3-} adsorption. Silica is less effective in absorbing PO_4^{3-} cations, therefore a coating is needed to increase the effectiveness of phosphate in wastewater [21].

Effect of different PEG concentration

The concentration of PEG in the solution the during coating process affects the performance of PEG-coated silica. The adsorption performance of PEG-coated silica is presented in Fig. 5.

Figure 5 shows variations in the concentration of PEG as a coating, and the optimal concentration for the adsorption of Fe and PO_4^{3-} is 15%. The higher the concentration of PEG, the higher the effectiveness of PEG in absorbing Fe and PO_4^{3-}. This is because the higher the

adsorbent concentration, the more active sites that can adsorb ions [22].

Effect of coating temperature

Fig. 6 shows the effect of coating temperature during synthesis of PEG-coated silica on the removal of phosphate and iron in wastewater. The higher the temperature, the higher the effectiveness of PEG-silica in adsorbing Fe and PO_4^{3-}. Optimal adsorption of Fe and PO_4^{3-} occurs at 50°C of coating temperature. At 60°C, the adsorption decreases because the active sites on the adsorbent surface are completely occupied. Higher temperature causes a decrease in the viscosity of the solution; this makes molecules easily transferred from the solution to and surface of the adsorbent [23]. Research conducted by [24] we investigated the adsorption and hence removal of lead II shows that temperature dramatically affects the ability of silica to adsorb ions.

CONCLUSIONS

PEG-coated silica has shown good adsorption of anions and cations in wastewater, in particular phosphate and iron ions. Based on the assessment of its adsorption efficiency, the optimal conditions for the coating process are 30 min, 50°C, with PEG to silica ratio of 1:3 and a PEG

concentration of 15%. PEG-coated silica can be used as an effective adsorbent of phosphates and iron in wastewater. It is suggested to apply this adsorbent to other anions and cations in wastewater for future research.

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