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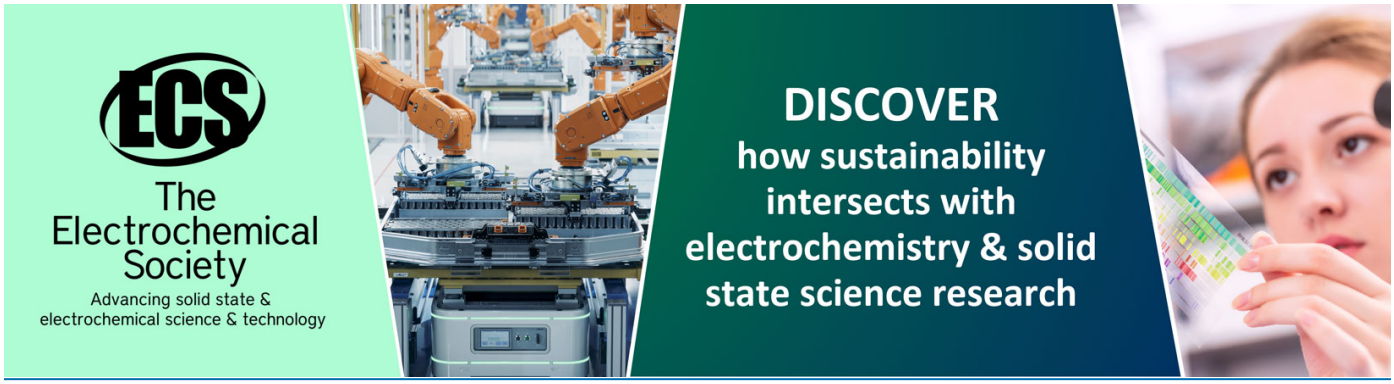

Synthesis of $ZnFe_2O_4$ Nanoparticles with PEG 6000 and Their Potential Application for Adsorbent

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Abstract. In general, about 10-15% of the dyes used in the colouring process in the textile industries are wasted into the waters. Though the dye waste is generally resistant, it is difficult to decompose, and toxic. One effort to process the waste before being discharged into the environment is the adsorption process. The process requires superior adsorbents of which main requirement is to have a large specific surface area, chemically and thermally stable, and also easily isolated from the system. One of the adsorbents that meet these requirements is zinc ferrite nanoparticles ($ZnFe_2O_4$), which is a magnetic nanometer-scale material that is thermally and chemically stable. Various methods of synthesis of $ZnFe_2O_4$ nanoparticles have been developed, one of which is coprecipitation. This method is a simple method but often produces polydisperse particles. The use of templates in the synthesis process is expected to overcome this problem. For this reason, the purpose of this study was to synthesize the $ZnFe_2O_4$ nanoparticles by coprecipitation using a PEG 6000 as a template. It was followed by the performance test of these materials as adsorbents for malachite green which is one of the dyestuffs often used in industry. The data analysis showed that PEG increased the crystallinity, specific surface area and monodispersity of $ZnFe_2O_4$. The results of VSM analysis showed that $ZnFe_2O_4$ without PEG had a magnetic value greater than $ZnFe_2O_4$ with a PEG template. In the malachite green adsorption test, the adsorption capacity of $ZnFe_2O_4$ with PEG was higher than the bar one that was equal to 16.7 mg/g.

Keywords: $ZnFe_2O_4$, nanoparticle, PEG, template, adsorbent

1. Introduction

The textile industry is the oldest industry that is currently growing rapidly. One of the industry's main ingredients is dyestuff. Approximately 10-15% of the dyes used in the coloring process cannot be reused and must be discharged into the aquatic environment [1]. If sewage treatment is not carried out properly, then the presence of dyestuff waste which is generally resistant has the potential to disrupt ecosystem balance both directly and indirectly.

Green malachite is a cationic dye often used as a dye for silk, wool, leather, cotton, and paper fabrics, and food coloring. Liquid waste green malachite substances in the waters interfere with photosynthesis

in the aquatic environment and cause damage to the liver, gills, kidney, and intestines of marine animals [2]. Consuming fish contaminated with these dye wastes can irritate the digestive system. Excessive green lazy dyes in the body of living things can also affect the immune system, reproductive system, and are carcinogenic [3]. Therefore, it is necessary to develop effective waste treatment methods before being discharged into the environment.

Several methods that have been developed to treat green malachite in liquid waste include coagulation, oxidation, ozonation, and adsorption [4]. Of these methods, an adsorption method is often an option. Adsorption is the simplest and cheapest method [5]. For this reason, superior adsorbents are needed, namely, adsorbents that have a large specific surface area, thermal and chemical resistance, and are easily isolated from the system so that they can be recycled. Various types of adsorbents have been developed, including activated carbon [6], zeolite [7,8], silica gel [9], chitosan [10,11], and bentonite [12]. However, the adsorbent often used in the process of dye waste processing is activated carbon. Activated carbon can reduce the dye content effectively, even though the adsorbent extraction, after the adsorption process takes place, becomes a problem [13].

One of the adsorbent extraction processes after the adsorption process takes place easily when magnetic adsorbents are used, is magnetite nanoparticles. Another advantage of this nano-scale material is its large surface area, so the adsorption capacity is also significant. However, this material has one drawback that is easily oxidized, especially at high temperatures [14]. Therefore, the development of magnetic adsorbents that have high stability is still needed. One of them is the development of zinc ferrite nanoparticles ($ZnFe_2O_4$) which can be used as an adsorbent. The $ZnFe_2O_4$ nanoparticles are one of the spinel ferrites which have better chemical and thermal stability [15]. The $ZnFe_2O_4$ nanoparticles can be synthesized by a hydrothermal method [16], solvothermal [17], and sol-gel [18]. However, this method is complicated to be developed on a large scale because it is expensive, complicated, requires sophisticated equipment, high reaction temperatures, long production times, and toxic reagents that are harmful to the environment [5]. An alternative method that can be seeded is the coprecipitation method. The coprecipitation method is often an option because it is relatively much simpler than other methods. Another advantage of the coprecipitation method is that it is easy, the time needed is relatively shorter, and can be used for large-scale nanoparticle production.

The $ZnFe_2O_4$ nanoparticles with a uniform size can be obtained by modified coprecipitation, for example by adding surfactants [19] and using complexing agents [20]. In addition, modifications are also intended to improve chemical and thermal stability, and dispersity. One complexing agent that can be used is polyethylene glycol (PEG). For this reason, the $ZnFe_2O_4$ was modified by coprecipitation with the addition of PEG 6000. The synthesized particles were then tested for adsorption capacity for GM. PEG 6000 has several advantages, namely stable, hygroscopic (easy to absorb and release moisture), and efficiently binding material. PEG 6000 acts as a complexing agent (template) that wraps or coats nanoparticles and inhibits or reduces interaction between particles so that agglomeration does not occur and obtains particles with a uniform shape that can increase dispersity and surface area.

2. Methods

The equipments used in this study were glassware, evaporation plates, mortar and pastel, thermometer, stopwatch, centrifuge, oven, hotplate, furnace, digital balance, XRD (Panalytical Xpert Pro) instruments, SEM-EDX (Type Inspect S50, FEI), FT-IR (Shimadzu Type FT-IR 8400S), BET (Nova 1200, Quantachrome), VSM (Oxford VSM 1, 2 H), cuvette, spectronic 20 (Genesys, Single Beam), shaker, shaker waterbatch. The materials used include whatmann paper, universal indicator (Merck), PEG 6000 (Merck), NaOH (Merck), acetone (Merck), $Zn(CH_3COO)_2 \bullet 2H_2O$ (Merck), $FeCl_3 \bullet 6H_2O$ (Merck), distilled water, demineralized water (Hydrobath), and green malachite.

2.1. Synthesis of $ZnFe_2O_4$ nanoparticles

The synthesis of $ZnFe_2O_4$ nanoparticles began by dissolving $Zn(CH_3COO)_2{\bullet}2H_2O$ and $FeCl_3{\bullet}6H_2O$ respectively into the demineralized water, mixing them so that the mole ratio of Fe:Zn is equal to 2:1. Then, NaOH solutions in the demineralized water was heated to a temperature of 75 °C. In the NaOH solution, the mixture from the above solution was added with constant stirring for 3 hours. In synthesis with the addition of PEG, the mixture was carried out alternately with an aqueous solution of PEG 6000 in a certain concentration. After stirring for several hours, the mixture was allowed to stand and cool at room temperature, and then the mixture was centrifuged for 1 hour so that centrifugates and brown deposits were obtained. The precipitate was then washed with the demineralized water until the pH of the filtrate was neutral. The residue was then ovenized at 80 °C for 8 hours, after it was pounded with mortar and pastel, and then furnished at 350 °C for 3 hours. The synthesis results in the form of brown powder were then characterized by XRD (X-Ray Diffraction), SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-Ray), FTIR (Fourier Transform Infrared), BET (Brunauer-Emmett-Teller), and VSM (Vibrating Sample Magnetometer).

2.2 Application of $ZnFe_2O_4$ nanoparticles as an adsorbent of green malachite

The samples were added into a certain concentration of aqueous solution of Green Malachite. The adsorption process was carried out by stirring the mixture with a shaker with a speed of 150 rpm on the variation of the contact time of 15, 30, 45, 60, 75, 90, 120, and 180 minutes. The mixture was then centrifuged for 15 minutes at a speed of 3000 rpm to separate centrifugates and deposits. The absorbance of the centrifugates was measured under λ_{max} of Green Malachite. The adsorption process was also carried out with variations in adsorbate concentration and temperature. The percentage of dyes adsorbed was calculated based on the results of the absorbance of the dye solution before (A_o) and after adsorption (A_t) with the equation (1). Meanwhile, the adsorption capacity was calculated by equation (2).

$$\text{Adsorbed Quantity (\%)} = \frac{(A_0 - A_t)}{A_0} 100\ \% \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_o is the initial concentration of green malachite (mg/L), C_t is the final concentration of green malachite (mg/L), q_t is the adsorption capacity (mg/g), V is the volume of green malachite solution (L), and $m$is the mass of $ZnFe_2O_4$ (g).

3. Results and Discussion

The result obtained at the end of the synthesis process was brown powders which was ready to be characterized by XRD, FTIR, SEM-EDX, BET, and VSM instruments. After that, the powder was tested for its ability as an adsorbent of a solution model of green malachite.

3.1. XRD Characterization

The XRD characterization results are presented in Figure 1. There is a match between the diffraction pattern of the synthesized material (both synthesized without or with the addition of PEG) with the ZnFe2O4 standard XRD pattern, JCPDS Card No. 22-1012, namely the presence of peaks at 29.86°; 35.21°, 43.6°, 53.20°, 57,3°, 62.25°. It means that the zinc ferrite nanoparticles have been successfully synthesized.

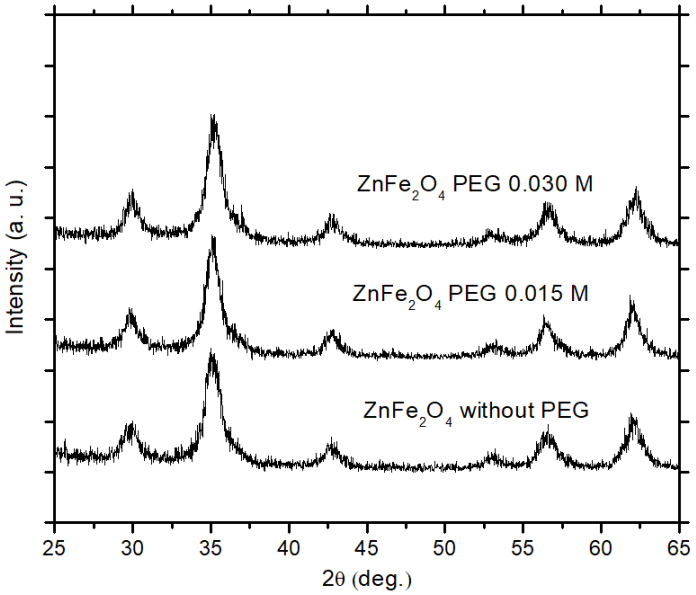

Figure 1. XRD spectra of $ZnFe_2O_4$ nanoparticles.

There was an increase in XRD peak intensity in the addition of PEG 6000 but it seemed insignificant. PEG facilitates crystal maturation. The regularity of the crystal structure increases with the addition of PEG. The effect of PEG concentration on the crystallinity of particles still needs to be studied further. The effect of adding PEG to the crystal size can be known by using the Debye-Scherrer equation as follows (equation 3).

$$D = \frac{K\,\lambda}{\beta \cos\theta} \qquad (3)$$

where D is the crystal grain size (nm), K is the Scherrer constant (0.9), λ is the X-ray wavelength (in Å), β is the width half peak (in radians), θ is the Bragg diffraction angle (in radians).

From Scherrer's calculation, the average crystallite size of $ZnFe_2O_4$ nanoparticles without PEG 6000 was 25.25 nm and the average crystallite size of particles with PEG 6000 at concentrations of 0.015 and 0.030 M were 13.13 and 11.48 nm, respectively. It means that PEG decreased the size of the nanoparticles. PEG acts as a template for crystal formation. The average crystallite size of zinc ferrite crystals with different PEG concentrations did not appear to differ significantly. However, because the concentration range used in this study was limited, the effect of PEG concentration on the average crystal size has not been concluded.

3.2. FTIR Characterization

The FT-IR spectrum of $ZnFe_2O_4$ nanoparticles without and with the PEG template is shown in Figure 2. Figure 2 shows the presence of absorption bands at wave numbers of 480-590 cm^{-1} indicating the presence of Fe-O and Zn-O bonds from $ZnFe_2O_4$ nanoparticles formed. The spectrum showed that there was no typical absorption band from PEG 6000, namely at the peaks associated with OH, CH, CO, and COC bond which is a type of PEG 6000 polymer constituent bond, because PEG 6000 was decomposed at 50-60 °C becomes CO_2 and H_2O gas so that in this study PEG 6000 was lost and proven as a template. Based on Figure 2, there appears to be no significant difference in intensity between zinc ferrite synthesized with and without the addition of PEG. The results of the characterization with FTIR reinforce the evidence of the success of zinc ferrites synthesis process.

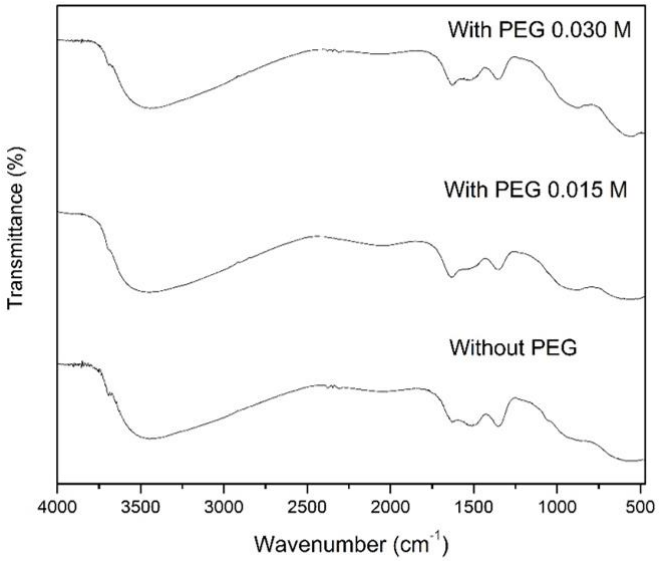

Figure 2. FTIR spectra of $ZnFe_2O_4$ nanoparticles.

3.3. SEM-EDX Characterization

From the SEM characterization that obtained Figure 3a and Figure 3b, it appears that the particle size ranged from less than 100 nm. It means zinc ferrite nanoparticles have been successfully synthesized. The synthesized particles with or without PEG showed spherical morphology. However, particles produced by PEG addition appeared more uniform. Meanwhile, the EDX spectrum produced a comparison of the composition of the number and mass of atoms in the $ZnFe_2O_4$ nanoparticles.

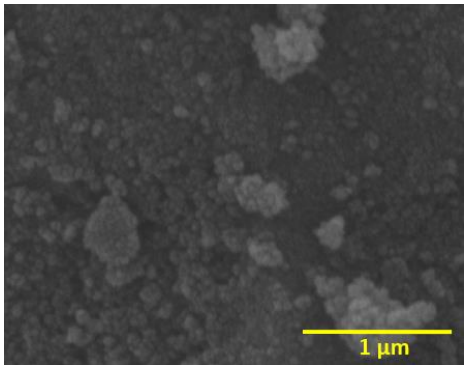

Figure 3a. SEM image of $ZnFe_2O_4$ nanoparticles without PEG.

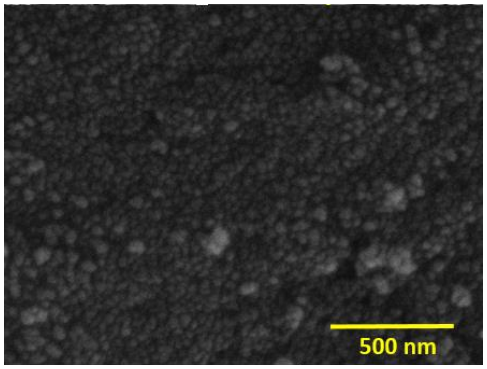

Figure 3b. SEM image of $ZnFe_2O_4$ nanoparticles with PEG.

The EDX analysis obtained qualitative and quantitative data. The qualitative data describes the types of elements constitute of the synthesis results. The quantitative data are in the form of a percentage of atoms (% At) and mass (% Wt). Based on these data, it was obtained an empirical formula prediction that corresponded to $ZnFe_2O_4$ nanoparticles. The EDX quantitative data are shown in Table 1.

Table 1. The composition of atoms of the $ZnFe_2O_4$ nanoparticles

Element	Without PEG		With PEG	
	Wt(%)	*At(%)*	*Wt(%)*	*At(%)*
Zn	28.21	15.07	28.13	15.03
Fe	46.06	28.79	46.17	28.87
O	25.57	56.14	25.70	56.11

Based on the EDX results as shown in Table 1, the particles synthesized without PEG had a ratio of Zn:Fe:O atomic percentages of 1:1.91:3.73. Meanwhile, the synthesized particles with PEG template had a ratio of Zn:Fe:O atomic percentages of 1:1.92:3.73. Slightly, it deviated from a ratio of 1:2:4; it was likely due to the formation of nanoparticles that were less than perfect or had crystal defects. However, the closest rounding produced the expected atomic percentage ratio, namely Zn:Fe:O 1:2:4. This evidence confirms the conclusion that $ZnFe_2O_4$ nanoparticles have been successfully synthesized.

3.4. BET Characterization

Characterization by the BET method was carried out to determine the specific surface area of $ZnFe_2O_4$ nanoparticles. The results of the characterization obtained the specific surface area values of $ZnFe_2O_4$ nanoparticles without PEG of 69.150 m^2/g and with PEG templates at concentrations of 0.015 M and 0.030 M respectively 98.324 m^2/g and 111.093 m^2/g. The presence of the PEG template can enlarge the specific surface area due to the smaller, more uniform size of the particles, and an opening of the pore after the PEG leaves the particle surface.

3.5. VSM Characterization

VSM characterization was carried out to determine the magnetic value of the $ZnFe_2O_4$ nanoparticles. The data obtained in the form of zinc nanoparticles magnetization curves without and with PEG are shown in Figure 4. It shows that the saturation magnetization value of zinc ferrite nanoparticles without PEG was greater than that of zinc ferrite nanoparticles with PEG 6000 template. Its is influenced by the particle size. The synthesized particles without PEG are agglomerated, so the particle size is greater. The larger the particle size, the harder the material is magnetized. Thus, the value of saturation magnetization is higher than the smaller size material.

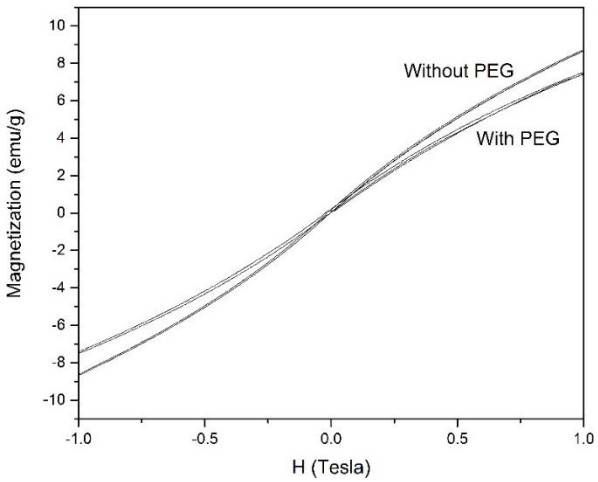

Figure 4. Hysteresis curve of $ZnFe_2O_4$ nanoparticles

3.6. Application of $ZnFe_2O_4$ nanoparticles as Green Malachite

The determination of the adsorption power of zinc ferrite from green malachite synthesis was carried out by measuring the concentration of dyes before and after the adsorption process by spectrophotometry below the maximum green malachite wavelength, which was 617 nm. The relationship between concentration and absorbance of the solution is determined by a standard curve. The adsorption process was carried out in varying contact times and temperatures.

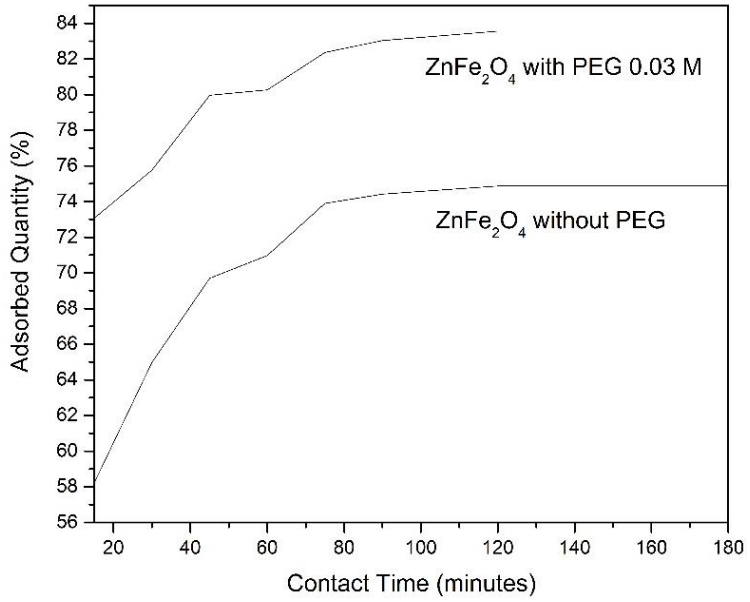

Figure 5. Hysteresis curve of $ZnFe_2O_4$ nanoparticles.

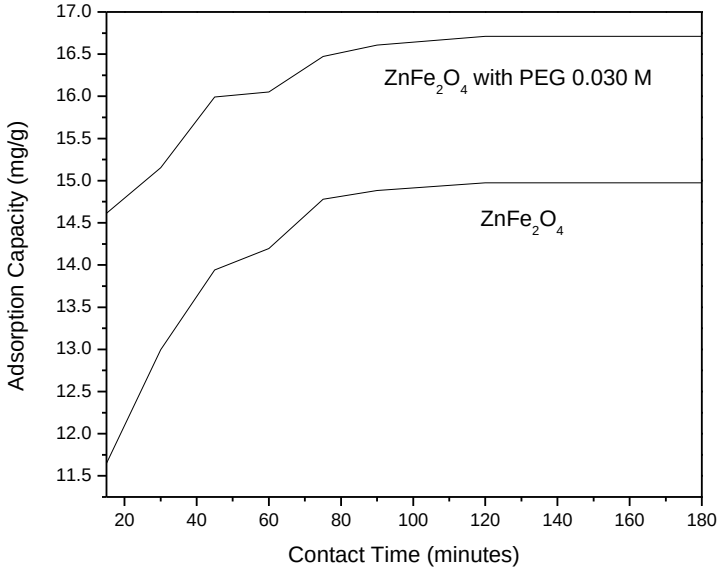

Figure 6. Hysteresis curve of $ZnFe_2O_4$ nanoparticles.

Figure 5 and Figure 6 show that the percent quantity of dyes and adsorption capacity of $ZnFe_2O_4$ nanoparticles increases with increasing contact time of adsorption until obtaining the optimum contact time. Based on the data obtained, the $ZnFe_2O_4$ nanoparticles with PEG template had a greater adsorption capacity than $ZnFe_2O_4$ nanoparticles without PEG. The greater the PEG concentration, the adsorption capacity was greater as well. The percentage of green malachite adsorbed by zinc ferrite with PEG 0.03 M was 83.558% which resulted in an adsorption capacity value of 16.712 mg/g. Table 2 describes the effect of temperature on the adsorption quantity and capacity for various initial concentrations. Table 2 shows that at various initial concentrations, the higher the temperature, the percentage of green lazy is adsorbed and the adsorption capacity will decrease. It is an indication that this adsorption process includes physical adsorption.

Table 2. Adsorption quantity and capacity for various temperature and initial concentration of $ZnFe_2O_4$ nanoparticles.

C_0 (mg/L)	C_e (mg/L)			Adsorption Quantity (%)			q_e (mg/g)		
	35 °C	45 °C	55 °C	35 °C	45 °C	55 °C	35 °C	45 °C	55 °C
11	0.933	1.442	1.712	91.522	86.891	84.440	20.135	19.116	18.577
12	1.449	1.637	2.049	87.921	86.361	82.928	21.101	20.727	19.903
13	1.839	1.959	2.805	85.854	84.932	78.421	22.322	22.082	20.390

4. Conclusion

The $ZnFe_2O_4$ nanoparticles with and without PEG have been successfully synthesized by coprecipitation. Based on the characterization by the BET method, the specific surface area of zinc ferrite nanoparticles without PEG was 69.150 m^2/g and with PEG 0.015 and 0.030 M respectively were 98.324 and 111.093 m^2/g. The EDX results obtained the empirical formula of the $ZnFe_2O_4$ nanoparticles and the VSM results obtained the magnetic value of $ZnFe_2O_4$ without PEG which was higher than $ZnFe_2O_4$ with PEG. The adsorption capacity of zinc ferrite nanoparticles is affected by contact time. The longer the contact time, the adsorption capacity increased. At 120 minutes contact time, the particles could adsorb 83.558% of adsorbate and its adsorption capacity was 16.712 mg/g. At various initial concentrations, the higher the temperature, the percentage of green lazy adsorbed and the adsorption capacity decreased. It is an indication that this adsorption process includes physical adsorption.

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