Nanostructural Properties of Fe$_{3-x}$Zn$_x$O$_4$-PEG/ Carboxymethyl Cellulose/ Polyvinyl Alcohol Magnetic Hydrogel by Using SAXS

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Abstract. The Fe$_{3-x}$Zn$_x$O$_4$-PEG/Carboxymethyl Cellulose/Polyvinyl Alcohol (Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA) magnetic hydrogel has been successfully synthesized through the freezing-thawing process. The filler of Fe$_{3-x}$Zn$_x$O$_4$ nanoparticles has been successfully fabricated using the coprecipitation method. The investigation of nanostructural characteristic of Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA magnetic hydrogel was conducted using X-Ray Diffractometer (XRD), TEM, and Small Angle X-ray Scattering (SAXS) spectrometer to analyse the structure of crystal, morphology of Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA nanoparticles, and nanostructural behaviour of Fe$_{3-x}$Zn$_x$O$_4$ distribution in the Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA magnetic hydrogel. The addition of Zn doping into Fe$_{3-x}$Zn$_x$O$_4$ nanoparticles with the variation of compositions of $x = 0.65, 0.75,$ and $0.85$ has been done and caused the shifting of the peak of diffraction angle to the smaller diffraction angle as the addition of $x$ composition. Through the X-ray analysis, it can be found that the sizes of Fe$_{3-x}$Zn$_x$O$_4$ nanoparticles crystal in the Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA magnetic hydrogel were around 10 - 12 nm. These data were in line with the data analysis using SAXS, especially the value of secondary particles from the Fe$_{3-x}$Zn$_x$O$_4$ filler with the values of about ~ 9 nm. Meanwhile, the values of Fe$_{3-x}$Zn$_x$O$_4$ primary particles were about ~ 2 nm. The data of the distribution of Fe$_{3-x}$Zn$_x$O$_4$-PEG magnetic nanoparticles in the Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA magnetic hydrogel were also supported by the characterization of the nanoparticles filler morphology using TEM showing the number of about 9 - 11 nm. The tissue of PEG/CMC/PVA polymer was effective enough in inhibiting the aggregation of Fe$_{3-x}$Zn$_x$O$_4$ filler nanoparticles so that they could be equally distributed in the Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA magnetic hydrogel.

Keywords: Fe$_{3-x}$Zn$_x$O$_4$, magnetic hydrogel, CMC, PVA, PEG 6000

1. Introduction
Magnetic nanoparticles are one of essential materials in the fabrication of liquid magnetic and hydrogel. The Magnetic hydrogel is the combination of magnetic characteristic resulted from magnet filler and elastic characteristic of hydrogel matrix [1]. Magnetic hydrogel material can be developed and utilized
in the biomedical and industrial fields such as drug delivery system [2], sensors [3], artificial muscles [4], hyperthermia therapy [5] and the others. To know and fix the behavior of magnetic hydrogel, the synthesis of nanoparticles filler and the selection of matrix polymer material are still developed by many researchers. Besides, the study on nanoparticles filler in the magnetic hydrogel is one of the ways to know and increase the effect of magnetic filler on the magnetic characteristic, magneto-thermal, and magneto-elasticity of the magnetic hydrogel.

In the study on the thermal characteristic, Maciel et al. [6] successfully fabricated the magnetic hydrogel composite based on iota-carrageenan with the maghemite filler. The maghemite filler was equally distributed all over the surface of hydrogel and resulted in the very good thermal stability of magnetic hydrogel composite. The selection of natural polymer as the magnetic hydrogel matrix was also reported by Paulino et al. [7]. They successfully fabricated magnetic hydrogel based on natural polymer using magnetite filler. The resulted magnetic hydrogel has the potential to be a controller of medicine release; this indication is shown by the amount of magnetic susceptibility resulted by that material. The amount of magnetic susceptibility is the contribution of the concentration of magnetite filler equally distributed all over the surface of the magnetic hydrogel. The study on magnetite filler nanostructure was also successfully reported by Sunaryono et al. [8]. They synthesized magnetite with the raw material of iron sand and fabricated the magnetic hydrogel based on polyvinyl alcohol (PVA) natural polymer. Magnetite filler underwent aggregation controlled in the tissue of PVA polymer hydrogel from the range of filler diameter between 13 nm and 32 nm as the function of the increase in the concentration of magnetite filler from 1% to 15% of the magnetic hydrogel weight. However, the study on the distribution of magnetite filler doped with Zn in the magnetic hydrogel based on Polyvinyl Alcohol (PVA) and Carboxymethyl Cellulose (CMC) is rarely reported.

The selection of Zn doping and PEG surfactant material in the synthesis of Fe\textsubscript{3-x}Zn\textsubscript{x}O\textsubscript{4} PEG nanoparticles aimed to study the aggregation behavior of magnetic filler in the Fe\textsubscript{3-x}Zn\textsubscript{x}O\textsubscript{4} PEG/CMC/PVA magnetic hydrogel. PEG is a surfactant polymer that is often used in drug delivery system since it has a high solubility level when it is in the water, no immunogenicity, and good biocompatibility [9]. When PEG easily dissolves in the body liquid, the material covered with PEG polymer will be automatically equally distributed in the body. The hydrogel matrix used in this research was the combination of CMC and PVA polymers. CMC polymer can increase the stability of a certain particle caused by hydroxyl cellulose tissue followed by the presence of carboxymethyl functional group [10]. Besides, CMC polymer can be easily hydrolyzed by cellulose enzyme in the form of simple glucoses and the bacteria can be fermented by ethanol [11]. Generally, CMC is a polymer that is economical enough and easily soluble in the water solution [12]. Meanwhile, PVA polymer is a polymer that has high hydrolysis degree, high biocompatibility, and good chemical resistance [13], and it is nontoxic so that it is suitable for the application of drug delivery [10]. Thereby, the combination of CMC and PVA polymers is very effective in fabricating magnetic hydrogel which is functional and multifunction.

2. Methods

2.1. Synthesis of Fe\textsubscript{3-x}Zn\textsubscript{x}O\textsubscript{4} PEG nanoparticles

The raw material used in this research was local iron sand taken from Sine Beach, Tulungagung, East Java. Such raw material was then purified to result in Fe\textsubscript{3}O\textsubscript{4} by dispersing using a permanent magnet. The Fe\textsubscript{3}O\textsubscript{4} particles as the results of separation were then dissolved in HCl (12 M) during 20 minutes and followed by a filtering process. The solution of the filtering result was mixed with ZnCl\textsubscript{2} (with three different variations), PEG polymer, and dropped with NH\textsubscript{4}OH (6,5 M). This process was carried out on a hot plate magnetic stirrer and spun for 30 minutes until the precipitation product was black. The precipitation result was leached repeatedly until reaching the pH 7 with distilled water. Finally, the precipitation product was filtered with the filter paper that left Fe\textsubscript{3-x}Zn\textsubscript{x}O\textsubscript{4} PEG powder.
2.2. Fabrication of Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA Magnetic Hydrogel

Fabrication of hydrogel was done by mixing CMC/PVA polymer matrix into the water with the comparison of 23:100 at the range of temperature of 70-90°C for one hour. Subsequently, the hydrogel was mixed with Fe$_{3-x}$Zn$_x$O$_4$-PEG powder and stirred until the mixture homogeneous. The result of the mixture was molded and the freezing-thawing process was carried out repeatedly so that the intended gel was formed. The magnetic hydrogel was then characterized using XRD X’Pert Pro Panalytical with the specification of the wavelength of 1.5406 Å and the range angle of 10°-80° and Small Angle X-ray Scattering (SAXS) with the specification of SDD 1200 mm until 4200 mm. The data analysis using XRD and SAXS was undertaken using Software Rietica, Origin 8, and Sasfit. To know the morphology of the particle size and confirm the distribution of Fe$_{3-x}$Zn$_x$O$_4$-PEG particles in the Fe$_{3-x}$Zn$_x$O$_4$-PEG/CMC/PVA magnetic hydrogel, the magnetic hydrogel was characterized using TEM.

3. Results and Discussion

The results of characterization using XRD from the Fe$_{3-x}$Zn$_x$O$_4$-PEG nanoparticle filler were analyzed through the software reitica and origin. All four samples of Zn$_x$Fe$_{3-x}$O$_4$-PEG nanoparticles with the variation of x = 0, 0.65, 0.75, and 0.85 corresponded to the model data of AMCSD of 0002400, AMCSD 0000945, AMCSD 0002402, and AMCSD 0002400, respectively. Besides, the Fe$_{3-x}$Zn$_x$O$_4$-PEG nanoparticles were analyzed using Rietveld method to know the lattice parameter and crystal structure referring to some model data such as AMCSD 0000945 (model data with inverse spinel structure), AMCSD 0002402 (model data with normal spinel structure), and AMCSD 0002400 (model data with mixing spinel structure). Based on the refinement results, the peak of diffraction of Fe$_{3-x}$Zn$_x$O$_4$-PEG crystal nanoparticles underwent a little bit shifting. The shifting of the crystal diffraction peak could be seen from the position of the diffraction angle of Fe$_{3-x}$Zn$_x$O$_4$-PEG as shown in Table 1. Moreover, all diffraction peaks on the hkl Fe$_{3-x}$Zn$_x$O$_4$-PEG corresponded to the data of characteristic of spinel structure diffraction pattern [15].

Table 1. Analysis of diffraction peak position of Fe$_{3-x}$Zn$_x$O$_4$-PEG crystal by adding the Zn dopant fraction

| No. | Sample                  | Diffraction peak position of the crystal on the hkl |
|-----|-------------------------|-----------------------------------------------------|
|     |                         | [220] | [311] | [222] | [400] | [422] | [511] | [440] |
| 1   | Fe$_2$O$_3$-PEG         | 30.18 | 35.34 | 42.81 | 53.32 | 56.91 | 62.35 | 71.22 |
| 2   | Fe$_{2.35}$Zn$_{0.65}$O$_4$-PEG | 30.01 | 35.25 | 42.78 | 53.28 | 56.87 | 62.29 | 71.14 |
| 3   | Fe$_{2.25}$Zn$_{0.75}$O$_4$-PEG | 30.17 | 35.41 | 42.13 | 53.43 | 56.87 | 62.45 | 70.96 |
| 4   | Fe$_{2.15}$Zn$_{0.85}$O$_4$-PEG | 30.04 | 35.27 | 42.13 | 53.28 | 56.87 | 62.45 | 71.14 |

Figure 1 shows that the highest diffraction peak in all samples of Fe$_{3-x}$Zn$_x$O$_4$-PEG occurred on the hkl 311. Through the data analysis using XRD, the shifting of the position of crystal diffraction peak angle, especially on the hkl 311 happened due to the doping of Zn$^{2+}$ ion in the magnetite sample. The Zn$^{2+}$ ion successfully entered the ferrite spinel structure of Fe$_2$O$_3$ to change the Fe$^{3+}$ ion. Interestingly, the effectiveness of the entering of Zn$^{2+}$ ion doping shown by the shifting of diffraction peak of Fe$_{3-x}$Zn$_x$O$_4$-PEG crystal to the lower diffraction angle occurred in the composition of x = 0.65 and x = 0.85. However, it was different from the composition of the fraction of x = 0.75. This case indicated that the limitation of doping fraction in the inverse spinel structure happened in the composition of the fraction of x = 0.75. This result is in line with the result reported by Zhang et al. [4]. In the inverse spinel structure, the substitution of Zn$^{2+}$ substituted the Fe$^{3+}$ in the stretching of the crystal axis, increased the space of the crystal state and cell volume [16]. This case was caused by the Zn$^{2+}$ ion tissue (74 pm) was higher than Fe$^{3+}$ ion tissue (64 pm) [17].
Besides, the behavior of Fe$_{3-x}$Zn$_x$O$_4$-PEG nanoparticles of which the shifting of the diffraction peak was toward the higher $2\theta$ and indicated the change in spinel structure in doping fraction of $x = 0.75$ [18]. There were two models of spinel data to analyze the change in the type of spinel when $x = 0.75$ toward $x = 0.85$ namely AMCSD 0002402 for the type of normal spinel and AMCSD 0002400 for the type of mixed spinel. When the parameter of the crystal (Bragg-R factor) for the model data of mixed spinel AMCSD 0002400 was lower than the model data of AMCSD 0002402, this case showed that such sample was more suitable for the mixed spinel structure ($x = 0.85$). Thereby, the shifting of the diffraction peak of normal spinel structure toward the inverse spinel occurred when the dopant fraction of $x = 0.75$. This phenomenon can be explained that Zn doping with $x = 0.75$ in the Fe$_3$ZnO$_4$ pushed the Zn$^{2+}$ in the octahedral position [19] and this case caused the tetrahedral position was saturated so that the composition of the spinel structure shifted from the normal spinel ($x = 0.75$) to the mixed spinel ($x = 0.85$). Through the equation of the composition of [Zn$_{1-x}$Fe$_x$]$^{2+}$][Zn$_x$Fe$_{3-x}$]$^{2+}$]O$_4$, the forming of mixed spinel by the distribution Zn$^{2+}$ definitely influenced the structural pattern of the samples [20]. The different finding was reported by the other research [18-19] namely the substitution of Zn in Fe$_3$O$_4$ formed the inverse spinel structure when the dopant fraction was $x < 0.4$. Thereby, the change of the normal spinel structural pattern to the inverse spinel or vice versa depended on the composition of dopant fraction and the domination of Zn$^{2+}$ ion in occupying both octahedral and tetrahedral positions.

**Table 2.** The results refinement of Fe$_{3-x}$Zn$_x$O$_4$-PEG nanoparticles using Rietveld method

| No. | Sample          | Rp   | Rwp  | $\chi^2$ | Bragg-R Factor | Model Data     |
|-----|-----------------|------|------|----------|----------------|----------------|
| 1   | Fe$_3$O$_4$-PEG | 20.52| 31.17| 1.41     | 5.23           | AMCSD 0002400  |
| 2   | Fe$_{2.25}$Zn$_{0.75}$O$_4$-PEG | 22.37| 30.90| 1.30     | 6.81           | AMCSD 0000945  |
| 3   | Fe$_{2.25}$Zn$_{0.75}$O$_4$-PEG | 22.81| 31.70| 1.39     | 7.24           | AMCSD 0002402  |
| 4   | Fe$_{2.15}$Zn$_{0.85}$O$_4$-PEG | 22.04| 30.89| 1.32     | 6.17           | AMCSD 0002400  |
Furthermore, to know the lattice parameter, particle size, diffraction peak profile, cell volume, \( dhkl \), and the structure of Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG, nanoparticles, this research conducted the refinement of XRD data using Rietveld method from some model data. Table 2 presents the analysis results of the parameters as the result of refinement. From Table 2, it is known that the parameter of refinement results had a good smoothing quality. This case was indicated by the data of Goodness of Fit (\( \chi^2 \)) that was approaching the value of 1 [23]. The information of these data can be the reference of discussion for the valid data. Meanwhile, the data analysis results in the form of lattice parameter, particle size, \( dhkl \), molecule weight, and cell volume are presented in Table 3.

Table 3. The lattice parameter of Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG nanoparticles crystal

| No. | Sample | \( a = b = c \) (Å) | Size (nm) | \( dhkl \) (Å) | Molecule weight | Cell volume |
|-----|--------|-----------------|----------|----------------|----------------|-------------|
| 1   | Fe\(_3\)O\(_4\)-PEG | 8.3631 | 12.56 | 12.48 | 2.315 | 1722.39 | 421.36 |
| 2   | Fe\(_{2.35}\)Zn\(_{0.65}\)O\(_4\)-PEG | 8.3522 | 12.28 | 12.25 | 2.323 | 1732.21 | 422.92 |
| 3   | Fe\(_{2.25}\)Zn\(_{0.75}\)O\(_4\)-PEG | 8.3734 | 10.45 | 10.97 | 2.359 | 1783.72 | 479.12 |
| 4   | Fe\(_{2.15}\)Zn\(_{0.85}\)O\(_4\)-PEG | 8.3804 | 10.39 | 10.15 | 2.361 | 1823.48 | 479.95 |

Based on Table 3, the size of Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG nanoparticles showed the corresponding values between data analysis using XRD with Rietica software and Debye Scherrer equation. The size of Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG nanoparticles obtained in the Rietica analysis was about 10.39-12.28 nm and in the calculation of Debye Scherrer was about 10.15-12.25 nm. To confirm the result of data analysis using XRD, this research also conducted a test using TEM instrument to know the morphology of Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG nanoparticles as shown in Figure 2. The data analysis by TEM using ImageJ software showed that the distribution of the sizes of Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG nanoparticles was in the range of 9.13-11.23 nm. This result highly corresponded to the result of data analysis using XRD.

Characterization using SAXS has been successfully carried out to know the characteristic of the nanostructure and the distribution of Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG nanoparticles filler in the Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG/CMC/PVA magnetic hydrogel. This characterization in this work focused more on the Fe\(_{3-x}\)Zn\(_x\)O\(_4\)-PEG nanoparticles filler with the composition of dopant fraction of \( x = 0.65 \). The data of SAXS as the results of characterization were analyzed using two lognormal distribution function to know the structure factor, form factor, and the parameters of nanoparticles distribution in the magnetic hydrogel. Besides, the model of two lognormal distributions also presented a certain information related to the distribution of primary and secondary particles [8]. Through the SAXS data, a number of a certain particle scattering (\( N \)) was used as a function of vector scattering (\( q \)) to calculate the scattering intensity. Besides, the data of analysis using SAXS were the combination between the scattering intensity \( I(q) \), structure factor \( S(q) \), and form factor \( P(q) \) of Fe\(_{2.35}\)Zn\(_{0.65}\)O\(_4\)-PEG nanoparticles in the Fe\(_{2.35}\)Zn\(_{0.65}\)O\(_4\)-PEG/CMC/PVA magnetic hydrogel per unit of volume. Such a relationship can be written as follow.
\[ I(q) = N_p P(q) S(q) + bkg \] (1)

The morphology of the samples in this experiment showed that the nanoparticles filler formed the fractal aggregate each another that involved the polydispersed nanoparticles (in the cluster size); by such aggregation, the distribution of the cluster size would be limited. Besides, the thing that influenced the different form between structure factor of single cluster and the observed one was polydispersity. The forming of the group such as fractal with \( \xi \) (correlation length) was in line with the sizes of all and \( D \) as the fractal dimension [24]. The structural factor in this system can be stated by the following equation [25].

\[ S(q, \xi, D, r) = 1 + \frac{D \Gamma(D-1) \sin \left( [D-1] \tan^{-1} (q \xi) \right)}{(q r_0)^D \left[ 1 + (q \xi)^{-2} \right]^{(D-1)/2}} \] (2)

The refinement of SAXS data of \( \text{Fe}_{2.35}\text{Zn}_{0.65}\text{O}_4\text{-PEG/CMC/PVA magnetic hydrogel} \) was analyzed through the SASfit software using two lognormal distribution function model shown by the profile of curve as shown by Figure 3. The two lognormal equation and the radius of primary and secondary particles were represented by \( R_1 \) and \( R_2 \) shown in equation 3 [26]. Based on the two lognormal analysis results, the sizes of \( \text{Fe}_{2.35}\text{Zn}_{0.65}\text{O}_4\text{-PEG} \) primary and secondary particles in the \( \text{Fe}_{2.35}\text{Zn}_{0.65}\text{O}_4\text{-PEG/CMC/PVA magnetic hydrogel} \) were 2.12 and 9.26 nm, respectively. These result correspond to the previous experimental report by Duan \textit{et al.} [20] and Lv \textit{et al.} [27]. They reported that the sizes of primary and secondary particles were \( \sim 2.2 \text{ nm} \) and 1-5 nm, respectively. By the data of the sizes of the \( \text{Fe}_{2.35}\text{Zn}_{0.65}\text{O}_4\text{-PEG} \) primary and secondary nanoparticles filler in the magnetic hydrogel, the aggregation occurred. The aggregation of \( \text{Fe}_{2.35}\text{Zn}_{0.65}\text{O}_4\text{-PEG} \) nanoparticles was the composition from 4 to 5 of the primary particles. Interestingly, the size of \( \text{Fe}_{2.35}\text{Zn}_{0.65}\text{O}_4\text{-PEG} \) secondary particles with the value of about 9.26 nm was well confirmed by the result of characterization using TEM and data analysis using XRD.

**Figure 3.** Profile of SAXS data of \( \text{Fe}_{2.35}\text{Zn}_{0.65}\text{O}_4\text{-PEG/CMC/PVA magnetic hydrogel} \)
4. Conclusion
The synthesis of Fe$_{1-x}$Zn$_x$O$_4$ nanoparticles with the variation of the composition of $x = 0, 0.65, 0.75,$ and 0.85 has been successfully conducted by the coprecipitation method. It corresponded to AMCSD 0002400 model data. The analysis of Fe$_{1-x}$Zn$_x$O$_4$-PEG nanoparticles was carried out using Reitica software and the obtained crystal sizes of Fe$_{1-x}$Zn$_x$O$_4$-PEG were about 10-12 nm. These data were well confirmed by the distribution of Fe$_{1-x}$Zn$_x$O$_4$-PEG in the Fe$_{1-x}$Zn$_x$O$_4$-PEG/CMC/PVA magnetic hydrogel through characterization using SAXS showing the values of Fe$_{1-x}$Zn$_x$O$_4$-PEG secondary particles were about $\sim 9$ nm. Through the two lognormal model data, the sizes of Fe$_{1-x}$Zn$_x$O$_4$-PEG primary particles were also about $\sim 2$ nm. It means that there were approximately 4 to 5 primary particles that aggregated to be the secondary particles. These results were strengthened by the results of characterization analysis using TEM showing the sizes of Fe$_{1-x}$Zn$_x$O$_4$-PEG nanoparticles were in the range of 9 - 11 nm and the data analysis using XRD that has been mentioned before.

References
[1] B. Saravanakumar, R. Mohan, K. Thiagarajan, and S.J. Kim, “Fabrication of a ZnO nanogenerator for eco-friendly biomechanical energy harvesting”, RSC Advances, vol. 3, no. 37, pp. 16646–16656, 2013.
[2] A. Mukhadis, S. Suhartadi, E. Sutadji, and P. Puspitasi, “Effectiveness of Professional Practice Work with Discovery Learning Methods in Engineering Program D IV Automotive Safety”, Advanced Science Letters, vol. 23, no. 2, pp. 1154–1157, 2017.
[3] Sunaryono et al., “Magneto-elasticity in hydrogels containing Fe$_3$O$_4$ nanoparticles and their potential applications”, 2013, pp. 53–56.
[4] Q. Zhang et al., “Muscle-like Artificial Molecular Actuators for Nanoparticles”, Chem, vol. 4, no. 11, pp. 2670–2684, Nov. 2018.
[5] M. M. Goswami, A. Das, and D. De, “Wet chemical synthesis of FePt nanoparticles: tuning of magnetic properties and biofunctionalization for hyperthermia therapy”, Journal of Magnetism and Magnetic Materials, Nov. 2018.
[6] D. J. Maciel, I. L. de M. Ferreira, G. M. da Costa, and M. R. da Silva, “Nanocomposite hydrogels based on iota-carrageenan and maghemite: Morphological, thermal and magnetic properties”, European Polymer Journal, vol. 76, pp. 147–155, Mar. 2016.
[7] A. T. Paulino et al., “Natural polymer-based magnetic hydrogels: Potential vectors for remote-controlled drug release”, Carbohydrate Polymers, vol. 90, no. 3, pp. 1216–1225, Oct. 2012.
[8] Sunaryono et al., “Contributions of TMAH Surfactant on Hierarchical Structures of PVA/Fe$_{1-x}$O$_x$–TMAH Ferrogels by Using SAXS Instrument”, J Inorg Organomet Polym, vol. 28, no. 6, pp. 2206–2212, Nov. 2018.
[9] S.J. Sung et al., “Effect of polyethylene glycol on gene delivery of polyethylenimine”, Biological and Pharmaceutical Bulletin, vol. 26, no. 4, pp. 492–500, 2003.
[10] A. Ayob, S. Alias, F. A. Dahalan, R. Santiagoo, A. Z. Abdullah, and T. T. Teng, “Kinetic removal of Cr$^{6+}$ by carboxymethyl cellulose-stabilized nano zeralvalent iron particles”, Macedonian Journal of Chemistry and Chemical Engineering, vol. 34, no. 2, pp. 295–308, 2015.
[11] H. Choi, J. R. Mitchell, S. R. Gaddipati, S. E. Hill, and B. Wolf, “Shear rheology and filament stretching behaviour of xanthan gum and carboxymethyl cellulose solution in presence of saliva”, Food hydrocolloids, vol. 40, pp. 71–75, 2014.
[12] G. Zi et al., “Catalytic hydrothermal conversion of carboxymethyl cellulose to value-added chemicals over metal–organic framework MIL-53 (Al)”, Carbohydrate polymers, vol. 115, pp. 146–151, 2015.
[13] P. Samanta, S. Bagchi, and S. Mishra, “Synthesis and Sensing characterization of ZnO nanofibers prepared by Electrospinning”, Materials Today: Proceedings, vol. 2, no. 9, pp. 4499–4502, 2015.
[14] Q. Nguyen, B. H. Kim, and J. W. Kwon, “based ZnO nanogenerator using contact electrification and piezoelectric effects”, *Journal of Microelectromechanical Systems*, vol. 24, no. 3, pp. 519–521, 2015.

[15] O. Acisli, A. Khataee, S. Karaca, A. Karimi, and E. Dogan, “Combination of ultrasonic and Fenton processes in the presence of magnetite nanostructures prepared by high energy planetary ball mill”, *Ultrasonics sonochemistry*, vol. 34, pp. 754–762, 2017.

[16] K. Ravichandran et al., “Tuning the combined magnetic and antibacterial properties of ZnO nanopowders through Mn doping for biomedical applications”, *Journal of Magnetism and Magnetic Materials*, vol. 358–359, pp. 50–55, May 2014.

[17] H. R. Rajabi, O. Khani, M. Shamsipur, and V. Vatanpour, “High-performance pure and Fe\(^{3+}\)-ion doped ZnS quantum dots as green nanophotocatalysts for the removal of malachite green under UV-light irradiation”, *Journal of Hazardous Materials*, vol. 250–251, pp. 370–378, Apr. 2013.

[18] J. P. Liu, E. Fullerton, O. Gutfleisch, and D. J. Sellmyer, *Nanoscale magnetic materials and applications*. Springer, 2009.

[19] J. Liu, Y. Bin, and M. Matsuo, “Magnetic Behavior of Zn-Doped Fe\(_3\)O\(_4\) Nanoparticles Estimated in Terms of Crystal Domain Size”, *The Journal of Physical Chemistry C*, vol. 116, no. 1, pp. 134–143, Jan. 2012.

[20] J. Zheng et al., “Mitigating Voltage Fade in Cathode Materials by Improving the Atomic Level Uniformity of Elemental Distribution”, *Nano Letters*, vol. 14, no. 5, pp. 2628–2635, May 2014.

[21] X. Duan, X. Wang, F. Yu, and D. Yuan, “Effects of Annealing Temperature and SiO\(_2\) Matrix on the Structure and Optical Properties of Co-Doped ZnAl\(_2\)O\(_4\)/SiO\(_2\) Nanoglass–Ceramic Composites”, *The Journal of Physical Chemistry C*, vol. 116, no. 3, pp. 2313–2321, Jan. 2012.

[22] X. Liu, J. Liu, S. Zhang, Z. Nan, and Q. Shi, “Structural, Magnetic, and Thermodynamic Evolutions of Zn-Doped Fe\(_3\)O\(_4\) Nanoparticles Synthesized Using a One-Step Solvothermal Method”, *The Journal of Physical Chemistry C*, vol. 120, no. 2, pp. 1328–1341, Jan. 2016.

[23] N. F. T. Braz et al., “Negative impact of high cumulative glucocorticoid dose on bone metabolism of patients with myasthenia gravis”, *Neurological Sciences*, vol. 38, no. 8, pp. 1405–1413, Aug. 2017.

[24] E. G. R. Putra, B. S. Seong, E. Shin, A. Ikram, S. A. Ani, and Darminto, “Fractal Structures on Fe\(_3\)O\(_4\) Ferrofluid: A Small-Angle Neutron Scattering Study”, *Journal of Physics: Conference Series*, vol. 247, p. 012028, Oct. 2010.

[25] Teixeira J., “Small angle scattering by fractal systems”, Proceeding Int Conf Appl Tech Small Angle Neutron Scatt. Argonne Natl Lab, Oct 26–29 1987:26–9.

[26] S. M. Yusuf et al., “Structural and magnetic properties of amorphous iron oxide”, *Physica B: Condensed Matter*, vol. 405, no. 4, pp. 1202–1206, Feb. 2010.

[27] Z. Lv et al., “Magnetic Behaviors of Mg- and Zn-Doped Fe\(_3\)O\(_4\) Nanoparticles Estimated in Terms of Crystal Domain Size, Dielectric Response, and Application of Fe\(_3\)O\(_4\)/Carbon Nanotube Composites to Anodes for Lithium Ion Batteries”, *The Journal of Physical Chemistry C*, vol. 119, no. 46, pp. 26128–26142, Nov. 2015.

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