Solvent Effect at Ibuprofen Adsorption Using Zinc Oxide Plate Rod-Like from Gelatine

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Abstract. The ubiquitous occurrence of several pharmaceuticals in sewage effluents has led to the considerable deterioration of some life forms and the quality of the receiving water bodies. Ibuprofen is a nonsteroid anti-inflammatory drug, represents a diverse class of drugs and the most commonly used analgesics for the management of pain and/or inflammation associated with rheumatoid arthritis and osteoarthritis, muscle stiffness and pain, dental pain, migraine, and headache. The present work investigated the effect of different solvents on ibuprofen dissolution during the adsorption of Ibuprofen on to zinc oxide plate rod-like from its hexane, methanol, ethanol solutions, and water as co-solvents. The zinc oxide plate rod-like was synthesized using block copolymer and gelatine as a template and zinc sulphate as zinc precursor was then characterized by X-ray diffraction, scanning electron microscopy, and FTIR to analyse the structure and morphology. The impact of various solvents on the percentage removal (%) of Ibuprofen was determined by batch adsorption experiments. The data obtained were subjected to isotherm and kinetic analysis to describe the distribution of ibuprofen between the liquid and solid phases in the batch studies. The results obtained best fitted the Langmuir isotherm model with an adsorption capacity close to 110mg/g at room temperature with an initial concentration of 100 ppm. To sum up, for large-scale removal, ibuprofen treatment for aquatic, zinc oxide plate rod-like maybe an adsorbent in future.

1. Introduction
At this time, there has been a lot of environmental pollution detected, especially in waters, for example in gutters, surfaces, and groundwater. Non-steroidal anti-inflammatory drugs (NSAIDs), such as ibuprofen, is pollutants that are harmful to the environment. Medication in drinking water can cause severe damage [1]. The presence of drugs in drinking water has adverse effects on human health and the ecosystem. Now, ongoing research to find more advanced ways to eliminate these contaminants is exploring submerged membrane bioreactors, coagulation and flocculation, activated sludge treatment, wet land construction, photocatalytic oxidation, catalytic ozonation, adsorption, advanced oxidation process, nanofiltration, biological processes, reverse osmosis, ultra-filtration, and etc [2]. However, this method still cannot be used effectively and economically to remove drug pollutants from water.

To get rid of these pollutants, effective treatment is needed. From this method, adsorption will be used because this method is the most promising. This process has been applied to eliminate organic compounds in drinking water treatment[3]. Adsorption method has several advantages including; Adsorption can handle various levels of pollutants, is efficient, easy to operate, is not affected by toxins, and is suitable for sustainable processes; The adsorbent can be regenerated and used repeatedly and has a low initial cost[4]. Heterogeneous photocatalysis with activated semiconductors, such as
zinc oxide (ZnO), is very possible for the process of decomposition of hazardous substances (pollutants) [5]. By using templates, such as zinc oxide, it is hoped that the adsorption process of ibuprofen can run optimally.

For solubility of ibuprofen, three variations of solvent will be used, namely n-hexane, methanol, and ethanol. From its nature, each one is different. N-hexane is the lightest solvent in lifting the oil contained in grains and is volatile, making it easier to reflux. This solvent has a boiling point between 65 and 70 °C and a dielectric constant of 1.89D [6]. Ethanol often used as a solvent in the laboratory because it has relatively high solubility, inert and does not react with other components. Ethanol has a low boiling point, making it easier to separate oil from its solvent in the distillation process. It has a boiling point of 79°C, a density of 0.789g/mL, and a dielectric constant of 24.30D [7]. While methanol is the most widely used solvent in the process of isolating the organic compounds of natural material, it has a boiling point of 65°C, a density of 0.791g/mL, and a dielectric constant of 33.60D [8]. When viewed from polarity, methanol is the most polar solvent compared with the other two solvents, so that the potential to obtain the best results from methanol solvents cannot be denied [9].

In this study, the formation of zinc oxide plate rod-like was investigated using Pluronic F127 with gelatin as a co-template through the hydrothermal method. Pluronic F127 is a soft organic template with a relatively high dissolution rate and low mechanical strength [10]. For the solubility of ibuprofen in the absorption process, three variations of solvents n-hexane, methanol, and ethanol will be used using the ratio between water and solvent, which is 100%water; 1:9; 5:5; 9:1; and 100% solvent. To know the effect of the variation and concentration of the solvent on the absorption of ibuprofen, the zinc oxide material was characterized using the X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and FTIR methods. For the large-scale removal of ibuprofen treatment from the aquatic body, zinc oxide plate rod-like may be an adsorbent in future.

2. Materials and Method

2.1. Synthesis of Zinc Oxide Plate Rod-Like
EtOH was dropped into the F127 solution using a burette (1 drop of EtOH per 20 seconds) at room temperature. After all, ethanol has been dropped, the mixture is stirred for 4 hours 150 rpm using closed conditions (crepe plastic). During dropping, no air enters by making a plastic crepe hole and covering the mouth with a mask. Gelatin is added then stirred for 60 minutes.

ZnSO₄ / Zn (NO₃)₂ drops in to the F127 with a burette (1 drop per 10 minutes) at room temperature. After everything was dropped, the mixture was stirred for 20 hours 150 rpm closed condition (crepe plastic) during the dripping process, no air enters by making holes in the crepe plastic and covering the mouth with the mixture put into the hydrothermal reactor then oven at 100 °C for 24 hours then cool, the white solid was filtered and washed with distilled water so that the pH = 7. The solid was dried at a temperature of 100 °C for 24 hours, and calcined at 550 °C for 12 hours, then the solid was stored in a clear bottle.

2.2. Characterization of Zinc Oxide Plate Rod-Like
The resulting sample will then be characterized using a Shimadzu 2100 brand Fourier Transform Infrared (FTIR) spectrophotometer resolution 0.5cm⁻¹, Scanning Electron Microscopy (SEM) ZEIS EVO MA 10, and X-Ray diffraction (XRD). This characterization aims to determine the size and morphology of the particles. Then the sample was applied in Ibuprofen adsorption.

2.3. Adsorption of ibuprofen on Zinc Oxide Plate Rod-Like
To find out the adsorption on a nanomaterial, ibuprofen solution was prepared in a solution of Water: Hexane in a ratio of 10: 0; 9: 1; 5: 5; 1: 9; 0:10 using 100 ppm concentration. The concentration of ibuprofen was monitored with a UV-Vis spectrophotometer at a wavelength of 291.5 nm. Calibration was done by preparing a standard solution of ibuprofen with a concentration of 5 to 100 ppm. Sixty mg of nano-ZnO was added to the ibuprofen solution and sterilized at room temperature for 60
minutes. A total of 3 mL of ibuprofen solution was taken at 5-minute intervals and then absorbance was measured using a Hitachi Japan UV-Vis U-2000 spectrophotometer. Then to determine the effect of the use of the solvent, the absorbent above process was carried out again using two other solvents, namely by replacing hexane to methanol and ethanol with the same concentration variations. The amount of ibuprofen absorbed by nano-ZnO is calculated using the equation,

\[ q_e = \left( C_0 - C_e \right) \left( \frac{v}{w} \right) \]  

(1)

\( C_0 \) is the initial concentration of ibuprofen, \( C_e \) is the equilibrium concentration of ibuprofen, \( v \) is the volume of the solution tested for its absorption, and \( w \) is the amount of zinc oxide plate rod-like used for adsorption.

3. Results and Discussion

3.1. Characterization of Zinc Oxide Plate Rod-Like

Using blocks copolymer and gelatin in the co-templating method, produced zinc oxide plate rod-like, and its morphology can be seen using SEM. Figure 1a shows the morphology of zinc oxide plate rod-like produced using block copolymer and gelatin at 2500x magnification. The zinc oxide plate rod-like material consisted of non-uniform structures, and the percentage of zinc obtained from EDX analysis is 76.6%. Following the introduction of gelatin at 1:0.05 of the block copolymer to gelatin weight ratio in the synthesis mixtures, the SEM analysis in Figure 1b shows zinc oxide plate rod-like at 10000x magnification. The SEM analysis in Figure 1b shows zinc oxide appeared in plate shapes with a diameter in the range of 1.2 ± 0.8 µm. The transformation between non-uniform structures to zinc oxide microspheres following the introduction of 0.05g of gelatin indicates the significant role of gelatin in directing the formation of zinc oxide structure. The SEM analysis proved that the presence of gelatin in the reaction mixture plays significant roles in directing the formation of microspherical zinc oxide and is also responsible for controlling the diameter of the zinc oxide plate rod-like.

![Figure 1](image1.png)

**Figure 1.** (a) Characterization results using SEM at 2500 × magnification, (b) Characterization results using SEM at 10000 × magnification

The XRD pattern on zinc oxide plate rod-like synthesized shown in Figure 2, the diffraction peaks of zinc oxide plate rod-like appeared at \( 2\theta = 27^\circ \) that corresponded to the diffraction of (001) plane. The (001) plane is significantly shifted to a higher diffraction angle when gelatin was used as co-template, suggesting lattice contraction that occurs due to the transformation from non-uniform zinc oxide to the microspherical structure. When plate rod-like of zinc oxides were produced at a low concentration of gelatin, high order geometric zinc oxide was formed based on a relatively small full width at a half-
maximum intensity of 001 plane. Changes in the concentration of gelatin also helped change the level of graphitization of zinc oxide as indicated by the decrease in intensity and FWHM from the peak, which shows the effect of gelatin in controlling the physical and chemical structure of zinc oxide plate rod-like.

**Figure 2.** Characterization results of Zinc Oxide Plate Rod-Like with XRD at 2 Tetha, 10-35° (left) and 35-60° (right).

The synthesized plate rod-like of zinc oxide were also characterized using infrared analysis. At Figure 3, the broad peak centred at 3429.58 cm⁻¹, which is corresponded to the stretching vibration of the hydroxyl group, were observed in all nanomaterials. Analysis of plate rod-like of zinc oxide synthesized using gelatin as co-template shows that the intensity of the hydroxyl functional group is significantly increased with the concentration of gelatin. The presence of hydroxyl on the surface reflects the number of terminals bonded to an oxygen atom, due to the formation of surface defects. The increase of surface hydroxyl species in nano plate rod-like of zinc oxide when increasing the amount of gelatin indicates the contribution of gelatin on the surface defects and also enhanced the functionality of zinc oxide. The residual functional groups from gelatin decomposition occurred on the surface of the nanoparticle, which generally occurred on materials produced via hydrothermal reaction.

**Figure 3.** Characterization results of Zinc Oxide Plate Rod-Like with FTIR at wavenumber (left) 3600-2500 cm⁻¹ and (right) 1200-500 cm⁻¹

### 3.2. Adsorption studies of ibuprofen on Zinc Oxide Plate Rod-Like
The potential use of plate rod-like of zinc oxide as an adsorbent for drug removal was investigated using ibuprofen as probe molecule with three solvent variations: methanol, ethanol, and n-hexane.
Figure 4 shows the absorption profile of ibuprofen on zinc oxide plate rod-like obtained from the variation of solvent (water:ethanol). High absorption of ibuprofen was observed on zinc oxide plate rod-like produced from water 100%. Figure 5 shows the adsorption profile of ibuprofen on zinc oxide plate rod-like obtained from the variation of solvent (water:methanol). High adsorption of ibuprofen was observed on zinc oxide plate rod-like also produced 100% from water. Figure 6 shows the absorption profile of ibuprofen on zinc oxide plate rod-like obtained from the variation of solvent (water:hexane). High absorption of ibuprofen was observed on zinc oxide plate rod-like produced from ratio water: n-hexane at 5:5. The absorption reached equilibrium at 330 min. Although infrared analysis revealed the high intensity of functional groups on the zinc oxide plate rod-like when increasing the concentration of gelatin, there is no significant enhancement on the absorption of ibuprofen. Meanwhile, the adsorption of ibuprofen is significantly influenced by the surface area and crystallite size of the zinc oxide plate rod-like. Kinetic analysis of ibuprofen absorption was carried out using linear regression analysis. Linear regression analysis is a quick and simple method applicable to a broad array of kinetic absorption systems. The best fit model is determined based on the $r^2$ and the obtained equilibrium value is compared with the experimental value in which the pseudo-second-order kinetic model is well fitted with the absorption of ibuprofen on plate rod-like of zinc oxide. Variations of solvents in the adsorption of Ibuprofen with zinc oxide plate rod-like uses several variations of solvents (methanol, ethanol, and n-hexane), which are shown in Figure 7.

![Figure 4. Absorption of ibuprofen using solvent: water and ethanol](image-url)
Figure 5. Absorption of ibuprofen using solvent: water and methanol

Figure 6. Absorption of ibuprofen using solvent: water and hexane

Figure 7 takes an example of the variation of solvents at ratio water:ethanol, methanol, and n-hexane of 1:9. Absorption high of ibuprofen was observed on zinc oxide plate rod-like resulting from water and hexane 9:1 ratio.
Figure 7. Ibuprofen absorption using solvent:methanol, ethanol and hexane ratio with water, 1: 9

In the curve, it can be seen that the methanol solvent is better than the two other solvents because it has the lowest Co/Ct, which means it has good absorption. Another reason is that methanol is also the most polar solvent compared to the other two, where the polariton methanol value is 33.60D, ethanol is 24.30D, and n-hexane is 1.89D. The character of the ibuprofen molecule as an organic molecule tends to dissolve easily in very polar solvents, such as methanol, because the interaction between polar-polar groups helps homogenization during absorption. The more polar the solvent, the faster it will dissolve the compound because ibuprofen can dissolve very easily in a solvent such as methanol. Not only facilitate dissolving, but methanol with short-chain clusters-OH will reduce the ibuprofen space barrier when interacting with the pore Zn plate to produce the highest absorption performance compared to the other two solvents.

4. Conclusion
Zinc oxide plate rod-like has been successfully synthesized using the hydrothermal method. The use of stem plates, such as zinc oxide, as an adsorbent in the absorption of ibuprofen is very dependent on the surface area and shape of ZnO. Effective absorption of ibuprofen is done using a variety of water:methanol and reaching equilibrium at 330 minutes. Methanol is selected as a better solvent compared to two other solvents, n-hexane and ethanol, because it has the lowest Co/Ct, which means it has good absorption. Another reason is that methanol is also the most polar solvent compared to the other two; methanol is more polar (33.60D) compared to ethanol (24.30D) and n-hexane (1.89D) because of the more polar the solvent, the faster it will dissolve compounds because ibuprofen can dissolve very easily in solvents such as methanol.

Acknowledgement
Authors acknowledge the Research Collaboration Indonesian Program (PPPKI) of SebelasMaret University 2019 under contract Number 1362/UN27.21/PN/2019 for Maria Ulfa.

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