

Ibuprofen Adsorption Study by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Models Using Nano Zinc Oxide from Mild Hydrothermal Condition

Abstract. Ibuprofen in the aquatic area as inflammatory drug residue is dangerous for environmental sustainability. The removal of ibuprofen at the aquatic area is carried out on nano zinc oxide (NZO) as an adsorbent. The NZO adsorbent was synthesized by gelatin self-assembly as a green method and characterized by FT-IR and XRD techniques. The residual ibuprofen model was prepared by dissolution of ibuprofen in water-hexane at ratio 10:0; 1:9; 5:5, 9:1 and 0:10. The optimized batch of experimental parameters were 100 ppm for 55 min at room temperature. Adsorption data was investigated by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. The result shows that Temkin model is the best model for describing the adsorption mechanism between ibuprofen as adsorbate and zinc oxide as an adsorbent. The adsorption capacity of 9:1 is the highest on that ibuprofen adsorption indicated that the composition of both solvents is favorable for ibuprofen dissolution due to polar-nonpolar interaction which is reaching 92% removal of ibuprofen. In the future, zinc oxide as adsorbent may be used for the removal of ibuprofen from any aquatic core area due to the economic and environmental reason.

1. Introduction

The presence of drugs in water is dangerous to humans and the environment. Ibuprofen is the drug which most often used by humans and found mostly in water. If the concentration in water is $> 1 \mu\text{g} / \text{L}$, it will endanger existing microorganisms, which can also affect the human health [1]. The presence of this drug in water can disrupt the balance of the ecosystem and the residue can modify the genetic information of natural bacteria so that resistance occurs [2]. Several ways have been used to reduce the concentration of ibuprofen in water such as ultrasonic irradiation [3], ozonation [4], chlorination [5], biodegradation [6], and adsorption [7]. Adsorption is the easiest and cheapest way to reduce the concentration of ibuprofen in water. However, the adsorption regeneration process is required when adsorption is needed. In addition, pollutants that have been adsorbed cannot be degraded into other compounds that are not harmful. Heterogeneous photocatalysis with activated semiconductors such as zinc oxide (ZnO) is very possible for the process of decomposition of hazardous substances (pollutants) [8]. By using nano-sized zinc oxide (nano-ZnO), it is expected that the adsorption process of ibuprofen can run optimally.

The adsorption data analysis in this study uses the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models. The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Freundlich model commonly used to describe the adsorption characteristics of the heterogeneous surface. The Temkin model assumes that the heat of adsorption (a function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage by ignoring the extremely low and large value of

concentrations. Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [9]

Based on the description above, a study of ibuprofen adsorption using nano-ZnO was carried out with adsorption data analysis using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models.

2. Materials and Method

2.1. Material

The chemical in this research are analytical grade. The material are zinc sulfate (ZnSO_4), ethanol (EtOH), F127, and gelatin as precursor and sulfuric acid as an activation solution.

2.2. Synthesis of ZnO

The ZnO synthesis was started by making 190 mL of ethanol solution with a ratio of ethanol and water 1: 3 then added to the 31-grams of ZnSO_4 base material. Then react with 3.6 grams of F127. Ethanol was dropped into the F127 solution with a burette (1 drop per 20 seconds) at room temperature. After all, ethanol has been dropped, the mixture is stirred for 2 hours 250 rpm closed condition (crepe plastic). When the drip is attempted, no air enters by making a drip hole in the crepe and covering the mouth with a mask. Then, the mixture was added with 0.0346 grams of gelatin and then sterilized for 60 minutes (solution A).

After that, ZnSO_4 solution was added to solution A with a burette (1 drop per 10 minutes) at room temperature stirrer conditions. After everything is dropped, the mixture is stirred for 20 hours 150 rpm closed condition (crepe plastic). During the dripping effort, there is no air entering by making holes in the plastic crepe and covering the mouth with a mask.

The mixture is put into a hydrothermal reactor while roasted at 100°C for 24 hours and then cooled. One other part is left at room temperature. After that the mixture is filtered, the solid is dried in an oven at 100°C for 24 hours then calcined at 550°C for 12 hours. Then the solids were stored in a clear, closed bottle.

2.3. Characterization of ZnO

The resulting sample will then be characterized using the Fourier Transform Infrared (FTIR) instrument brand Shimadzu 2100 resolution 0.5cm^{-1} 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.

2.4. Adsorption of Ibuprofen on nano-ZnO

To find out the adsorption on nanomaterial, ibuprofen solution was prepared in a solution of water: hexane in a ratio of 10:0; 9:1; 5:5; 1:9; and 0:10 concentrates of 100 ppm. 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. 60 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 minutes intervals and then absorbance was measured using a Hitachi Japan UV-Vis U-2000 spectrophotometer. The amount of ibuprofen absorbed by nano-ZnO is calculated using the equation

$$qe = (Co - Ce) \left(\frac{v}{w} \right) \quad (1)$$

Co is the initial concentration of ibuprofen, Ce is the equilibrium concentration of ibuprofen, v is the volume of the solution tested for its absorption, and w is the amount of nano-ZnO used for adsorption.

Changes in the concentration of adsorbate by the adsorption process in accordance with the mechanism of adsorption can be studied through the determination of the adsorption isotherm. The adsorption data analysis in this study uses the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models [10]

Langmuir equation: $\frac{1}{qe} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L} \times \frac{1}{Ce}$

Freundlich equation: $\text{Log } qe = \frac{1}{n} \text{Log } Ce + \text{Log } K_f$

Temkin equation: $q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e$

Dubinin-Radushkevich equation: $\ln q_e = \ln q_m - \beta \epsilon^2$

Where q_{max} , the monolayer capacity of the adsorbent (mg/g); KL , the Langmuir constant (L/mg) and related to the free energy of adsorption; q_m , the theoretical saturation capacity (mg/g); and ϵ , the Polanyi potential, which is equal to $RT \ln (1 + (1/C_e))$, where R (J/mol K) is the gas constant and T (K) is the absolute temperature; β , a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/kJ^2).

3. Result and Discussion

3.1. Characterization of nano-ZnO

Analysis of zinc oxide using X-Ray Diffraction is shown in Figure.1 Characterization result of nano-ZnO with 0-800. The XRD pattern on ZnO synthesized showed the diffraction peaks at $2\theta = 270$. When nano-ZnO were produced at low concentration of gelatin, high order geometric nanoparticle was formed based on relatively small full width at half maximum intensity of (002) plane. The graphitization degree of the nano-ZnO changed with the concentration of gelatin evident by the decrease in the intensity and FWHM of the peaks which indicates the influence of gelatin in controlling the physical and chemical structure of the nanoparticle.

The synthesized of ZnO were also characterized using infrared analysis. Figure 2 showed that the broad peak centered at 3750 cm^{-1} , which is corresponded to the stretching vibration of the hydroxyl group were observed in all nanomaterials based on [11] that compounds containing hydroxyl and carboxyl functional groups play a role in the formation of nanoparticles. The presence of surface hydroxyl reflects the number of terminals bonded to oxygen atom that may due to the formation of surface defects. The C=O group showed at 1600 cm^{-1} and the C-C group showed at 600 cm^{-1} . The vibration of ZnO can showed at 600 cm^{-1} which is corresponded to the literature that the vibration of metal with O group from ligand will show at $600\text{-}400 \text{ cm}^{-1}$ [12]

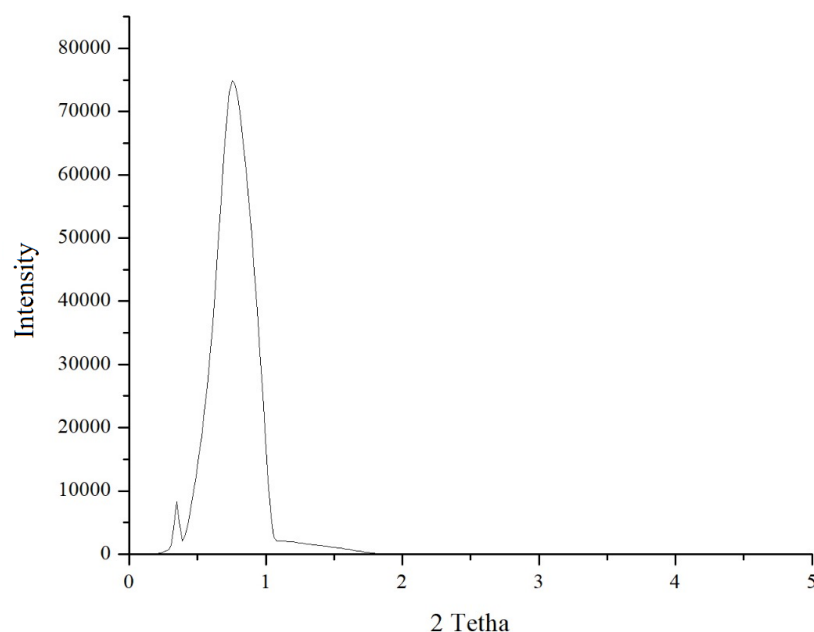


Figure 1. Characterization result of nano-ZnO in the scanning range 0-80°.

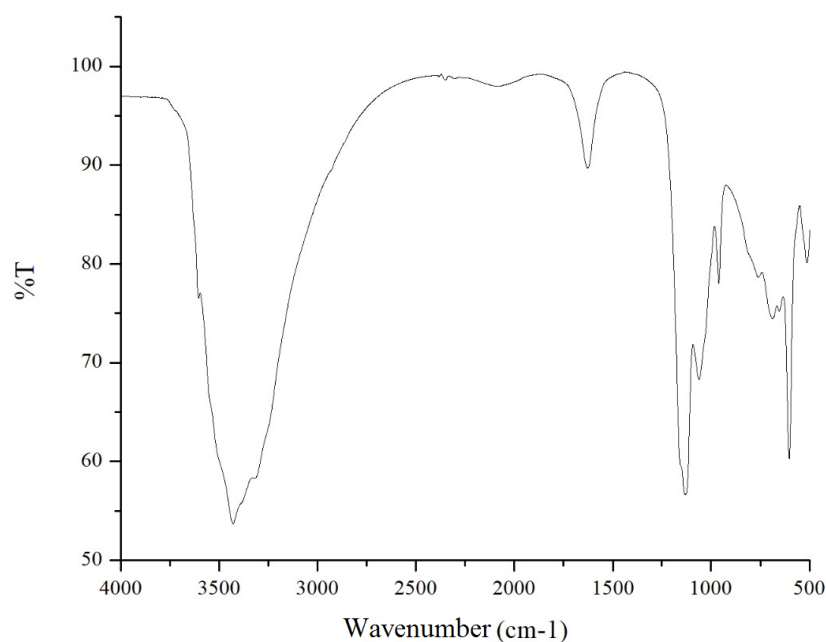


Figure 2. Characterization result of nano-ZnO with FTIR.

3.2. Adsorption studies of ibuprofen on nano-ZnO

The use of nano-ZnO as an adsorbent in the drug removal process has been carried out with ibuprofen as a molecule probe. Figure 3 shows the adsorption of ibuprofen with nano-ZnO using a variation of water solvent:hexane. The best absorption of ibuprofen is shown by variations of water solvents: hexane of 9:1. Adsorption experiences equilibrium in the 330 minutes. The adsorption of ibuprofen is significantly influenced by the ratio of solvent which is the component of hexane in water was increased not only the solubility of ibuprofen, but also the adsorption of ibuprofen molecules onto ZnO.

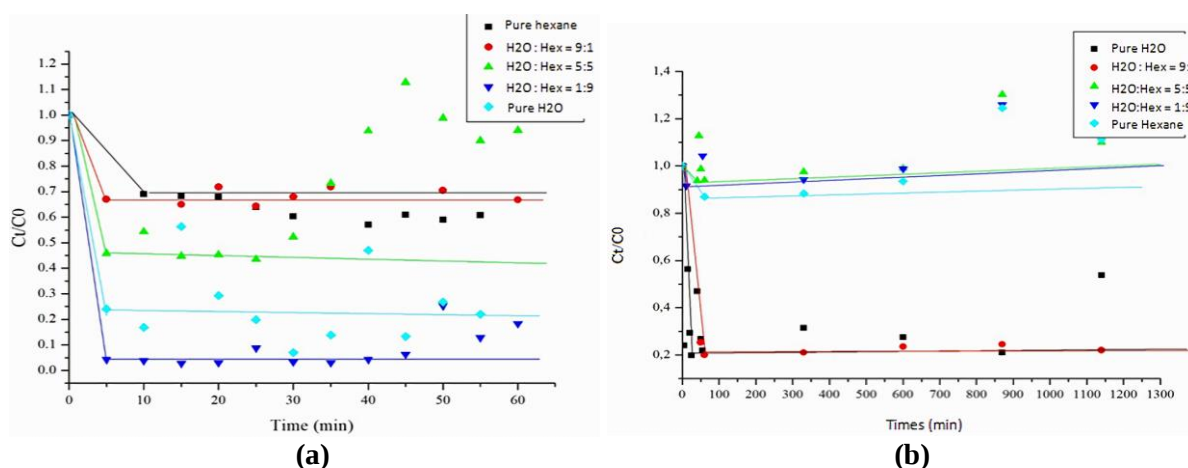


Figure 3. Adsorption of ibuprofen using a water solvent: hexane for (a) 60 minutes and (b) 1200 minutes.

Table 1. Isotherm analysis on ibuprofen adsorption using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models.

No	Model	Equation	R ²
1	Langmuir	$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L} \times \frac{1}{C_e}$	0.5688
2	Freundlich	$\log q_e = \frac{1}{n} \log C_e + \log K_f$	0.908
3	Temkin	$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e$	0.997
4	Dubinin-Radushkevich	$\ln q_e = \ln q_m - \beta \varepsilon^2$	0.8709

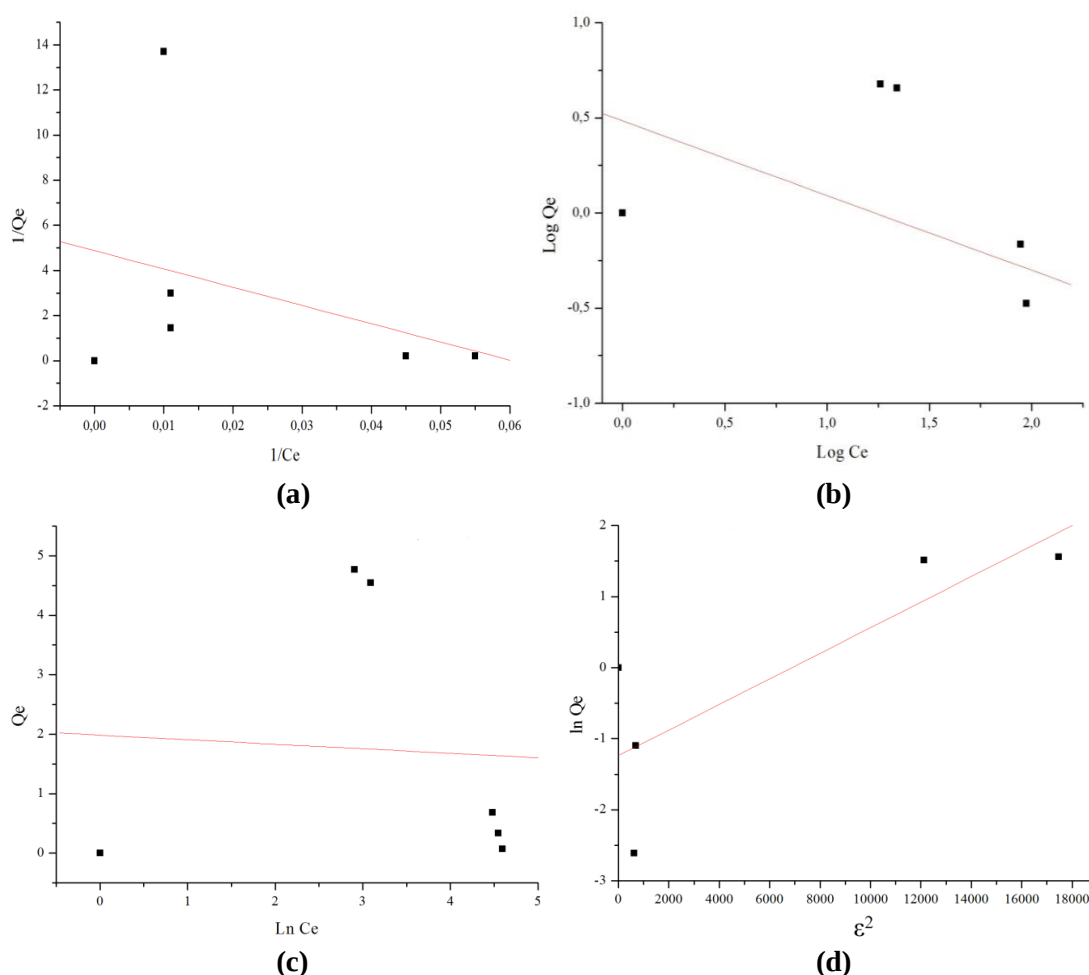


Figure 4. (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Dubinin-Radushkevich.

The best model to use is the Temkin model because $R^2 = 0,997$ is close to 1 and the largest among the three other models, namely R^2 Langmuir = 0.5688, Freundlich = 0.908, and Dubinin-Radushkevich = 0.8709, as shown in Table 1 and Figure 4. Temkin model takes into account the effect of adsorbate interactions on the adsorption process. It is also assumed that the heat of adsorption of all molecules in the layer decreases linearly as a result of increase surface coverage. This model confirms that the adsorption of ibuprofen onto zinc oxide follows a chemisorption process because the application of this model is for chemical adsorption [13]

4. Conclusion

Nano-ZnO has been successfully synthesized using the hydrothermal method. The use of nano-ZnO as an adsorbent in ibuprofen adsorption is highly dependent on the surface area and shape of ZnO.

Effective ibuprofen adsorption is performed with a water: hexane solvent with ratio of 9:1 and reaches an equilibrium point at 330 minutes. Isotherm analysis on ibuprofen adsorption is more effective using the Temkin model than the Langmuir, Freundlich, and Dubinin-Radushkevich models. So, the adsorption of ibuprofen onto nano-ZnO follows chemisorption process. And it could be conclude that nano-ZnO is a potential and active adsorbent for removal ibuprofen from the water.

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