Adsorption of Ciprofloxacin from solution on mesoporous silica MCM-48: Kinetic study

Cite as: AIP Conference Proceedings **2360**, 050043 (2021); https://doi.org/10.1063/5.0059487
Published Online: 28 September 2021

Miftahul Jannah, Paulina Taba, I. Wayan Sutapa, et al.

Adsorption of Ciprofloxacin from Solution on Mesoporous Silica MCM-48: Kinetic Study

Miftahul Jannah[1], Paulina Taba[1 a)], I Wayan Sutapa[2] and Yusafir Hala[1]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University, 90245, Makassar-Indonesia*
[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Pattimura University, Jl. Ir. Putuhena No. 1, Poka, Ambon-Indonesia, 90245*

[a)]Corresponding author: *paulinataba@unhas.ac.id*

Abstract. Antibiotics in the environment can affect biotic processes, cause resistance to microorganisms, and have an effect on human health. Ciprofloxacin (CIP) is one of the antibiotics that is found as a pollutant in the aquatic environment. In this study, MCM-48 was used as a material to remove CIP from the solution. Adsorption of CIP on MCM-48 achieved the equilibrium at 80 minutes. The pseudo-second-order is the most suitable kinetics model to describe the adsorption process with a correlation coefficient value of 0.9997 and a rate constant k_2 of 0.2684 g mg^{-1} min^{-1}.

INTRODUCTION

Antibiotic resistance is one of the threats to human health today. Antibiotic resistance is a condition when microorganisms are resistant to drugs that can kill or inhibit them. Antibiotic waste contamination is one of the factors that cause antibiotic resistance [1]. The presence of antibiotics in the environment can affect biotic processes and cause resistance to microorganisms even in small amounts [2]. Antibiotic contamination can come from pharmaceutical industrial waste [3]-[6] hospital waste [5-6] to livestock waste [6]. These wastes enter the environment and pollute rivers, fresh surface water [7], and drinking water [8]. The types of antibiotics that become contaminants also vary. Ciprofloxacin (CIP) one of antibiotic that is found as a pollutant in waters in various parts of the world. Antibiotic waste is generally treated conventionally by activated sludge or biodegradation methods, but it does not give satisfactory results. Research conducted by Tong et al [9] found that the activated sludge method was ineffective for removing ciprofloxacin waste. Therefore, we need another method that is cheap and effective to remove this waste in an aquatic environment.

One of the methods of eliminating antibiotics is adsorption. Adsorption has been proven to be one of the water treatment methods that are efficient, environmentally friendly, and easy to operate. The adsorption process is widely applied in industry to remove organic pollutants [10]. One of the materials commonly used is MCM-48. In general, mesoporous silica materials exhibit significant properties, such as large and uniform pore sizes (typically, in the range of 2-30 nm in diameter), high surface area, and pore volume [11]-[12],[19]. Synthesis of MCM-48 used a mixture of surfactants (cetyltrimethylammonium bromide, CTAB, and Triton X-100) as a template, as well as Ludox HS-40 as a source of silica. Characterization of MCM-48 obtained using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscope (SEM). The effect of parameters on CPI adsorption, such as contact time was investigated.

The 6th International Conference on Basic Sciences 2020 (ICBS 2020)
AIP Conf. Proc. 2360, 050043-1–050043-5; https://doi.org/10.1063/5.0059487
Published by AIP Publishing. 978-0-7354-4116-3/$30.00

METHODS

Materials

The materials used in this study were a cationic surfactant (CTAB), a neutral surfactant (Triton X-100) Ludox HS-40, ciprofloxacin ($C_{17}H_{18F}N_3O_3$), acetic acid (CH_3COOH), sodium hydroxide. (NaOH), hydrochloride acid (HCl), ethanol (C_2H_5OH). The last four reagents were from Merck. We used all analytical grade chemicals without any further purification.

Synthesis and Characterization of MCM-48

We synthesized MCM-48 using the previous procedure [13] with some modification [14]. There was no addition of sodium chloride as described in Ref. [13] and [14]. We characterized the obtained material by using an X-ray Diffractometer (XRD) ran at high degrees 2-theta, a Fourier Transfrom Infrared (FTIR) spectrometer scanned at a wavenumber range of 4000 – 340 cm^{-1}, and a scanning electron microscope (SEM) with a magnification of 10000x.

Effect of Contact Time on Adsorption of Ciprofloxacin

The experiment used to study the adsorption kinetics of CIP on MCM-48 were carried out at different contact times. The adsorbent of as much as 0.1 g was added into an Erlenmeyer containing 50 mL of 50 mg/L. We stired the mixture for a period of 3-200 minutes. All experiments for CIP adsorption were at room temperature. After being filtered, we measured the absorbance of CIP using a UV-Vis spectrophotometer at a maximum wavelength of 271 nm. A kinetic study used pseudo-first-order and pseudo-second-order models as given in Equation (1) and (2).

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1(q_e - q) \tag{1}$$

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2(q_e - q)^2 \tag{2}$$

The linear equation for the pseudo-first-order and the pseudo-second-order models is in Equations (3) and (4), correspondingly.

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

The rate constant for the former model is k_1, and for the later model is k_2. The amount of CIP adsorbed at equilibrium and at a contact time of t is q_e and q_t, respectively.

RESULTS AND DISCUSSION

Characterization of MCM-48

Fig. 1 shows the spectrum of MCM-48 obtained in this study. The absorption bands observed indicates the presence of -OH, -CH, and Si-O functional groups. The broad absorbance band at a wavenumber of 3344 cm^{-1} belongs to the -OH group. The absorption bands at wavenumbers of 2852 and 2922 are for C-H stretching vibrations supported by the peaks at wavenumbers of 1483 and 1471 cm^{-1} for C-H bending vibrations. The Si-O stretching vibrations are observed with intense bands at wavenumbers 1226 and 1064 cm^{-1}, as well as weak bands at 960 and 794 cm^{-1}.

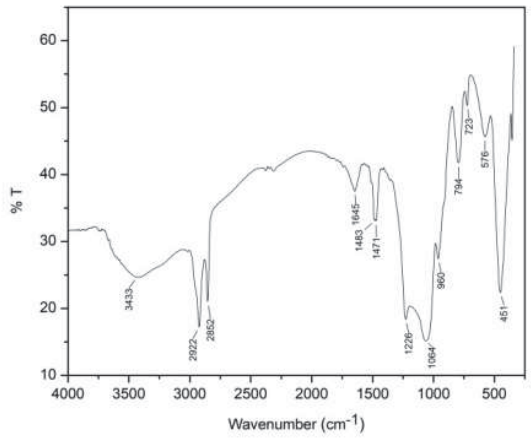

FIGURE 1. FTIR spectrum of MCM-48

Usually, the diffraction pattern of MCM-48 was observed at degrees 2θ of 1-10 °. However, in this study, the measurements were made starting from 15°. As shown in Fig. 2 XRD pattern of MCM-48 shows diffraction peaks at 18-22°. The diffraction pattern of MCM-48 obtained shows the area of the amorphous peak at degrees 2θ of 20-25°. Another research group reported the application of high angle to characterize MCM-48 in an X-ray diffractometer [15]. The results obtained were similar to the one in this study showing that the as-synthesized material is MCM-48.

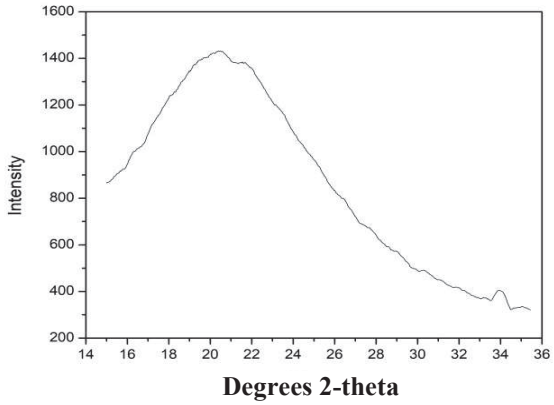

FIGURE 2. XRD Pattern of MCM-48

The morphology of the material is given in Fig. 3. The image shows the uniform shape of MCM-48 particles. This finding is consistent with the one reported previously [16].

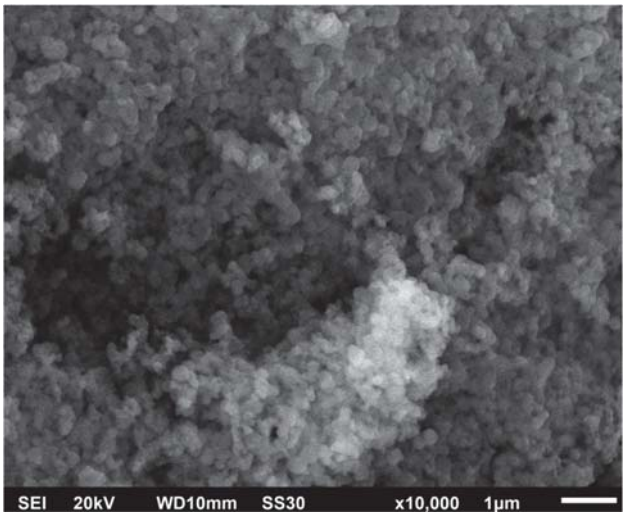

FIGURE 3. SEM image of MCM-48

Kinetics Study on Adsorption of Ciprofloxacin

The equilibrium time is the most important parameter in adsorption. Fig.4 shows that there was a rapid uptake of CPI within the first 80 min. After the contact time, the adsorption decreases. This phenomenon occurs because the sites on MCM-48 were still empty at the beginning of the adsorption. Therefore, the interactions between sites on MCM-48 and CIP are high. Over time, the sites on the MCM-48 continued to fill, and gradually large parts of the sites became saturated [17].

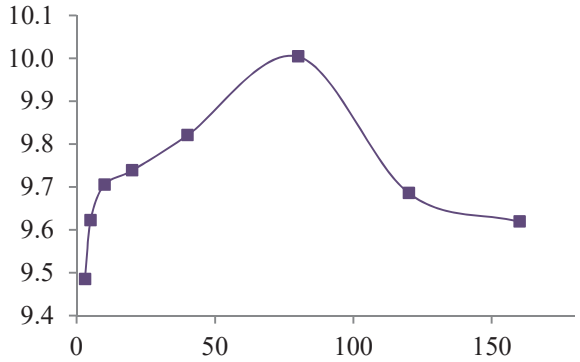

FIGURE 4. The Amount of CPI Adsorbed as a Function of Contact Time

The kinetic study is a valuable way to get information on the adsorption efficiency and the time estimated required for the entire process. Fig. 5 gives the kinetics study using the pseudo-first-order and pseudo-second-order modes. The R^2 value obtained by using a pseudo-first-order kinetics model for the adsorption of CIP by MCM-48 was 0.0233, whereas that for the pseudo-second-order kinetics model is 0.9997. The q_e value obtained from the pseudo-first-order kinetics model was 0.35 mg/g, and that from the pseudo-second-order kinetics model was 9.66 mg/g.

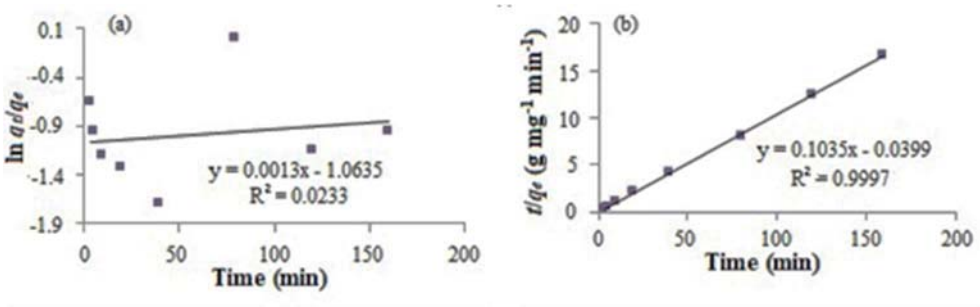

FIGURE 5. Pseudo-first and Pseudo-second-order kinetics models

The q_e value obtained from the experiment was 10 mg/g. the q_e value obtained from the pseudo-second-order kinetics model is closer to the q_e value obtained from the experiment than to the q_e value obtained from the pseudo-first-order. This finding shows that the adsorption of CIP by MCM-48 follows a pseudo-second-order kinetics model with a constant k_2 value of 0,27 g/mg.min. Another study has reported the same model for the CIP adsorption using a different adsorbent [18].

CONCLUSION

The adsorption of CIP from solution on MCM-48 has been studied. The adsorption of CIP on MCM-48 reached the equilibrium at 120 minutes. The experimental data showed a high correlation coefficient for the pseudo-second-order model in adsorbing CIP with a rate constant of 0.27 g mg^{-1} min^{-1}.

ACKNOWLEDGMENTS

It is our pleasure to thank the Ministry of Research Technology and Higher Education of Indonesia for funding the research through the master's thesis grant in 2020.

REFERENCES

1. Kraemer, S.A., Ramachandran, A. and Perron, G.G. *Microorganism.* **7**, 1-24 (2019).
2. S D Costanzo, J Murby, and Bates, Mar. Pollut. **51**, 218-223 (2005).
3. D G J Larsson , C Pedro, and N J Paxeous, Hazard. Mater. **148,** 751-755 (2007).
4. J Fick, H Söderström, R H Lindberg, C Phan, M Tyskllind, and D G J Larsson, Environ. Toxicol. Chem**. 28**, 2522-2527 (2009).
5. A Y C Lin, and T T Tsai, Sci. Total Environ. **407**, 3793-3802 (2009)
6. W J Sim, W J Lee, E S Lee, S K Shin, S R Hwang, J E Oh, *Chemosphere*. **82,** 179-186 (2011).
7. M Danner, A Robertson, V Behrends, and J Reiss, Sci. Total Environ. **664,** 793-804 (2019).
8. Z Ye, H S Weinberg, and M T Meyer, Anal. Chem. **79**, 1135-1144 (2007).
9. C Tong, X Zhuo, and Y Guo, J. Agric. Food Chem. *Food* **59**, 7303-7309 (2011).
10. N Sakkayawong, P Thiravetyan and W Nakbanpote, J. Colloid Interface Sci. **286,** 36-42 (2005).
11. T W Kim, F Kleitz, B Paul and R Ryoo, J. Am. Chem. Soc. **127,** 7601-7610 (2005).
12. Z S Mehdi, J. Biol. Chem. **3,** 63-74 (2015).
13. P Taba, Mak. Journ. Sains. **12,** 120-125 (2008).
14. J D M Diaz , G P Joya, J R Utrilla, R L Ramos, M S Polo, M A F Garcia and N A M Castillo, J. Colloid Interface Sci. **345,** 481-490 (2010).
15. Z Fei, S. Ai, Z Zhou, X Chen, J Tang, M Cui and Xu Qiao, J. I. Eng. Chem. **20,** 4146-4151 (2014).
16. H Aghaei, A A Nourbakhsh, S Karbasi, R j Kalbasi, M Rafienia, N Nourbakhsh, S Bonakdar and K J D Mackenzie, Ceram. Int. **40,** 7355-7362 (2014).
17. C Dube, R Tandlich and B Wilhelmi, Nova Biotechnol Chim. **17,** 16-28 (2018).
18. N Genc and E C Dogan, Desalination Water Treat. **53,** 785-793 (2015).
19. I.W. Sutapa, Rosmawaty, and H. Ropa, J. Phys.: Conf. Ser. **1341**, 032001 (2019).