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Feasibility of Ceria Nanocrystal Adsorbent for Amoxicillin Removal from Water

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Abstract. This study explored adsorptive property of ceria nanocrystal as an adsorbent for amoxicillin removal from water. Ceria nanocrystal was synthesized by employing precipitation method and characterized by using XRD and N_2 adsorption-desorption analysis. The adsorption experiment was performed by managing amoxicillin in natural condition. Then, parameters in the adsorption experiment, such as adsorbent dosage, contact time, temperature and initial concentration of amoxicillin are varied. The XRD pattern illustrated that the average crystallite size of ceria nanocrystal formation was 13.08 nm. N_2 adsorption-desorption analysis showed that ceria nanocrystal was mesoporous with specific surface area of 65.26 m^2/g. The amoxicillin adsorption of ceria nanocrystal adsorbent was described by Langmuir isotherm model with maximum adsorption capacity of 37.17 mg/g. The adsorption kinetic of ceria nanocrystal corresponded to the pseudo-second order model. Removal efficiency of amoxicillin by ceria nanocrystal was approximately 80% within 60 minutes over temperature range 303-323K. Those parameter results are described that ceria nanocrystal adsorbent is feasible as a rapid amoxicillin removal from water.

Introduction

Cerium oxide (ceria), a rare earth oxide is commonly used as catalytic converters (automotive exhaust) [1], UV blocking agent (sunscreen) [2], and antioxidant agent (medicine) [3,4]. It is also used as an effective adsorbent for heavy metals and dyes pollutants removal in wastewater treatment [5, 6, 7, 8, 9, 10]. However, only a few studies explored the potential of ceria nanocrystal for antibiotic removal in water [11].

A very large usage of antibiotics contributes to water pollution resulted in bacterial resistance increment, and poses threat to ecosystem sustainability. One proposed method for handling antibiotics in water is the adsorption process using activated carbon [12-15]. Pouretedal and Sadegh showed that amoxicillin is the most difficult antibiotics to eliminate using activated carbon compared to other antibiotics such as cephalexin, tetracycline and penicillin [12]. The practical applications of activated carbon are still limited due to expensive raw material and complex manufacturing processes [16]. Therefore, exploration of alternative adsorbent for antibiotics removal continues.

Ceria in nanoscale sized (ceria nanocrystal) is favourable for pollutants adsorption in water due to large surface area and high mobility in solution. These properties enable a quick whole solution volume cleaning. This study described the feasibility of ceria nanocrystal as an adsorbent for amoxicillin removal. First, ceria nanocrystal was synthesized using precipitation method from relatively inexpensive cerium nitrate. Next, ceria nanocrystal was analysed using various models to determine kinetic parameters and mechanism of amoxicillin adsorption behaviour.

Experimental

Materials. Cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) as cerium precursor was purchased from Sigma-Aldrich Ltd. Ammonium hydroxide (Merck) was used as precipitant. Demineralized water (DW) and iso-propanol (Merck) were utilized as solvent. Amoxicillin was obtained from Indonesian Pharmaceutical.

Synthesis and characterization. Ceria nanocrystal was synthesized by precipitation method as described in reference [4]. Cerium nitrate solution (0.08 M) was made by dissolving cerium nitrate with mixed solvent of DW and iso-propanol. Ammonium hydroxide was added into solution until pH 10 was achieved. The precipitate was dried at 373K for 3 hrs and calcined at 773K for 2 hrs to form crystalline of ceria nanocrystal. The structure of ceria nanocrystal was analysed using X-ray diffractometer (PANanalytical). The average crystallite size (*D*) and microstrain (η) were estimated using Williamson-Hall equation as [10]

$$\frac{\beta \cos\theta}{\lambda} = \frac{0.9}{D} + 4\eta\frac{\sin\theta}{\lambda} . \quad (1)$$

Where λ is x-ray wavelength, β denotes FWHM, and θ is diffraction angle. Specific surface area (SSA) and pore size distribution were calculated from the N_2 adsorption/desorption using multipoint Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halendra (BJH) method (Quantachrome Nova Instrument), respectively.

Adsorption experiment. The adsorption isotherm of amoxicillin was carried out with 20 mL amoxicillin solution (50 mg/L) and different amount of ceria nanocrystal (3 - 20 mg) to obtain optimum dosage of adsorbent. The mixture was stirred with the speed rotation of 300 rpm at room temperature in the dark condition. Experiment was performed for 60 min at pH ~ 5 as a natural condition of amoxicillin solution. Thus, adsorption equilibrium experiment was conducted with 15 mg of ceria nanocrystal and various concentration of amoxicillin solution (25-150 mg/L). For adsorption kinetic study, the experiment was taken with interval time 15-120 min in 50 mg/L amoxicillin solution. The samples were centrifuged at 6000 rpm for 10 min to separate adsorbent from solution. The residual of amoxicillin concentration was measured using UV-vis spectrophotometer (UV Vis 1240 Shimadzu) at 228 nm. In order to investigate the effect of temperature, adsorption experiment was performed in 50 mg/L amoxicillin solution at temperature 303, 313 and 323K. The removal efficiency η (%) of amoxicillin and adsorption capacity at contact time (*t*) of ceria nanocrystal were calculated using equations as follow:

$$\eta\,(\%) = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (2)$$

$$q_t = \frac{(C_o - C_t)V}{m}. \quad (3)$$

Where C_o (mg/L) and C_e (mg/L) represent the initial and equilibrium concentration of amoxicillin, C_t (mg/L) and q_t (mg/g) are concentration of amoxicillin and adsorption capacity at time (*t*), *V* (L) is volume of amoxicillin solution and *m* (g) denotes the mass of ceria nanocrystal.

Results and Discussion

Characterization of ceria nanocrystal. Figure 1(a) provides the XRD pattern of ceria nanocrystal. The identified diffraction peaks correspond to the cubic fluorite structure of cerianite (JCPDS:43-0394) which was consistent with other studies [4-10]. The size and microstrain were estimated using Williamson-Hall plot as shown in the insert of Fig 1(a). The obtained crystallite size was 13.08 nm and microstrain was 3 x 10^{-3} indicating the formation of ceria nanocrystal. N_2 adsorption/desorption isotherm measurement was used to calculate specific surface area and pore size of ceria nanocrystal. Fig. 1(b) exhibits hysteresis loop of N_2 adsorption/desorption isotherm of ceria nanocrystal. Based on the International Union of Pure and Applied Chemistry (IUPAC), the hysteresis loop identified as a type IV isotherm of mesoporous materials. The pore size distribution (insert in Fig. 1(b)) shows pore size of ceria nanocrystal in the range 1.66 – 62.16 nm. In addition, three peaks at 2.31 nm, 3.46 nm and 6.30 nm observed, which shows the existence of mesoporous in ceria nanocrystal. The analysis of BET specific surface area indicated that ceria nanocrystal possessed S_{BET} = 65.26 m^2/g which is comparable to other research findings [9].

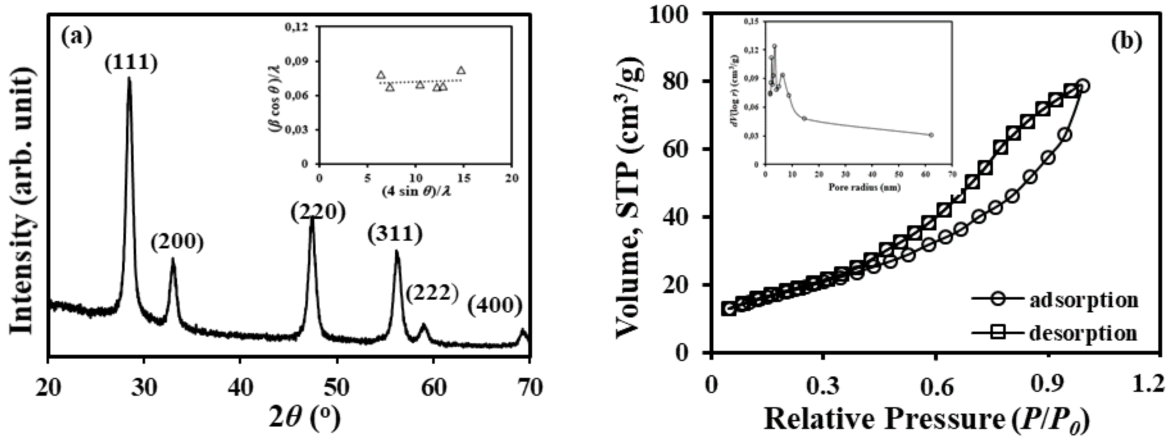

Fig. 1. (a). X-ray diffraction pattern and Williamson-Hall plot, (b). N_2 adsorption-desorption isotherm and the pore size distribution of ceria nanocrystal

Removal efficiency. The removal efficiency of amoxicillin for ceria nanocrystal with dosage of 3, 5, 10, 15 and 20 mg calculated using Eq.2. Fig. 2(a) depicts that removal efficiency of amoxicillin is risen as the amount of ceria nanocrystal is increased. The ceria nanocrystal amount of 15 mg yielded approximately 80% of the removal efficiency of amoxicillin. This result is higher than removal efficiency of amoxicillin using activated carbon [12]. The enhancement of ceria nanocrystal amount caused increase in surface area as active sites for adsorption [18]. Hence, it leads to the increment of adsorbed amoxicillin. However, the amount of ceria nanocrystal more than 15 mg did not result in an increase in removal efficiency. Hence, in this study 15 mg ceria nanocrystal was optimum dosage for adsorption of amoxicillin. In addition to the adsorbent dosage, temperature is also one of the parameters that affect removal efficiency. The removal efficiency of amoxicillin of about 80% achieved at temperature of 303, 313 and 323K as shown in Fig. 2(b). The temperature is insignificant affected on the removal efficiency. Similar result found on Cr(IV) adsorption on ceria nanosphere synthesized by hydrotermal process [6].

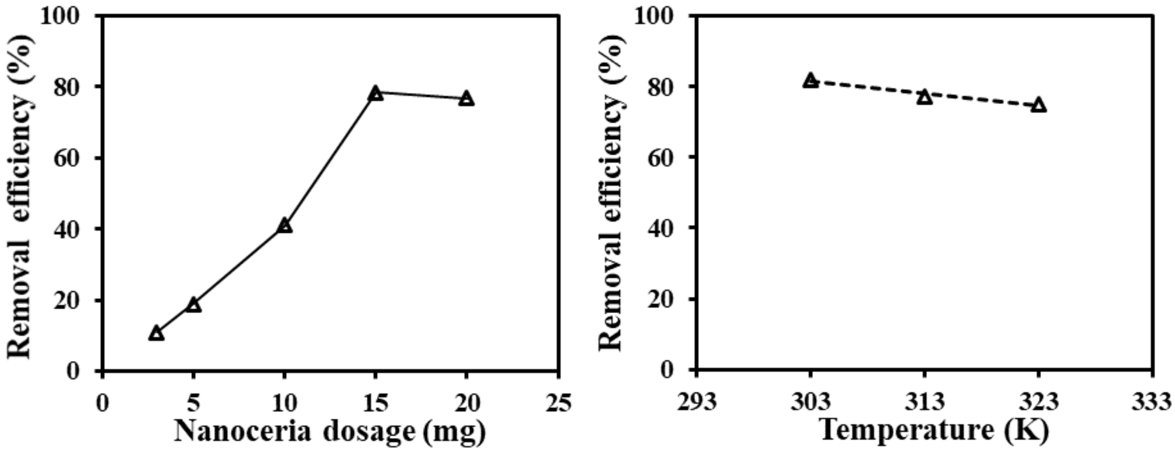

Fig. 2. Removal efficiency of amoxicillin for (a). Different ceria nanocrystal dosage, and (b). Different temperature (amoxicillin concentration 50 mg/mL, contact time 60 minutes)

Adsorption equilibrium. The adsorption equilibrium of amoxicillin on ceria nanocrystal surface was investigated based on removal efficiency which calculated for various contact time from 15 to 120 min by using Eq. 2. Fig. 3 exhibits the removal efficiency of amoxicillin as function of contact time. The adsorption process resulted in 52% removal efficiency of amoxicillin in the first 15 min. The removal efficiency increased up to approximately 80% in 60 min and then almost unchanged up to 120 min. The result showed that the adsorption rate rises rapidly at the beginning and increases moderately within 15 to 60 min. Finally, the adsorption rate increases slightly until 120 min contact time. The equilibrium achieved in 60 min indicating rapid adsorption of amoxicillin on ceria nanocrystal surface.

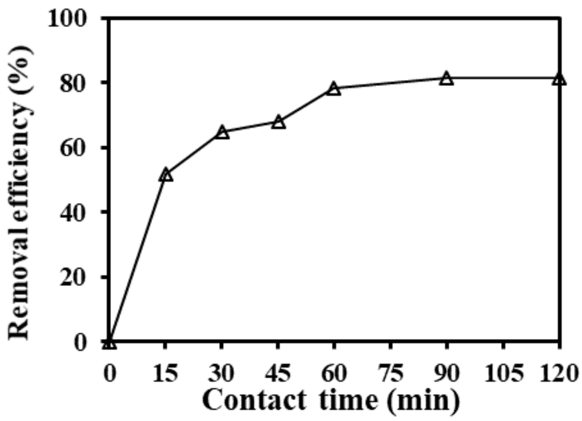

Fig. 3. Removal efficiency of amoxicillin versus contact time (amoxicillin concentration 50 mg/mL)

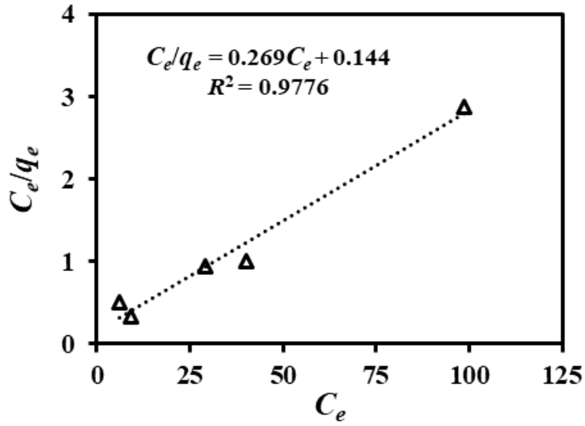

Fig. 4. Linear plot of Langmuir isotherm model for adsorption of amoxicillin on ceria nanocrystal

Adsorption isotherm. The adsorption experimental data fitting was performed to realize the application of ceria nanocrystal as an adsorbent for water pollutant treatment. Different adsorption isotherm models i.e. Langmuir, Freundlich, Temkin and Sips isotherm are mainly used to obtain suitable model that describes adsorption of amoxicillin on adsorbents [12-14,17]. In our study, adsorption of amoxicillin on ceria nanocrystal fitted well by Langmuir isotherm model. The linear form of Langmuir isotherm model represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} . \quad (4)$$

Where q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir isotherm constant. The linear plot of Langmuir isotherm model for adsorption of amoxicillin on ceria nanocrystal shown in Fig. 4. The Langmuir parameters (q_m and K_L) were obtained from the slope and the intercept of the vertical axis (Fig. 4). The value of q_m was found to be 37.18 mg/g which was closed to experimental data 39.96 mg/g, and the value of K_L was 0.187 (L/mg) with correlation coefficient (R^2) of 0.9776. The Langmuir isotherm model assumes monolayer adsorption on homogeneous sites [12-14]. Hence, the high value of correlation coefficient suggests that amoxicillin govern monolayer adsorbed on homogeneous surface of ceria nanocrystal. In addition, the feasibility of adsorption process determined by the essential isotherm characteristic of Langmuir model (R_L),

$$R_L = \frac{1}{1 + K_L C_o} . \quad (5)$$

The value of R_L determines the nature of adsorption process. The nature of adsorption is unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ or irreversible if $R_L = 0$. The calculated R_L value using Eq. 5 was 0.097. Based on the value of R^2 and R_L, our ceria nanocrystal is feasible for amoxicillin removal from water [12-14].

Adsorption kinetic. The adsorption kinetic represents the relation of adsorption capacity and contact time. The experimental data fitted using the adsorption kinetic models: the pseudo-first order, pseudo-second order and intra-particle diffusion model [12-15,17]. The fitting of experimental data corresponded to pseudo-second order model. The linear form of pseudo-second order model expressed by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

Where k_2 denotes the equilibrium rate constant of pseudo-second order (g/mg.min). The plot of Eq. 6 depicted in Fig. 5(a). The result shows correlation coefficient (R^2) closed to 1, suggesting that the experimental data is in a good agreement with the pseudo-second order model. The adsorption parameters obtained from the slope and intercept of the linear plot in Fig. 5(a). The value of equilibrium adsorption capacity (q_e) was 30.58 mg/g closes to the value of experimental data (27.61 mg/g). Meanwhile, the adsorption rate constant was 8.52 x 10^{-2} (g/mg.min). The adsorption rate constant is an important parameter to evaluate feasibility and efficiency of adsorbents. These results show that pseudo-second order is an appropriate model to describe adsorption mechanism of amoxicillin on ceria nanocrystal [5,8,12-14].

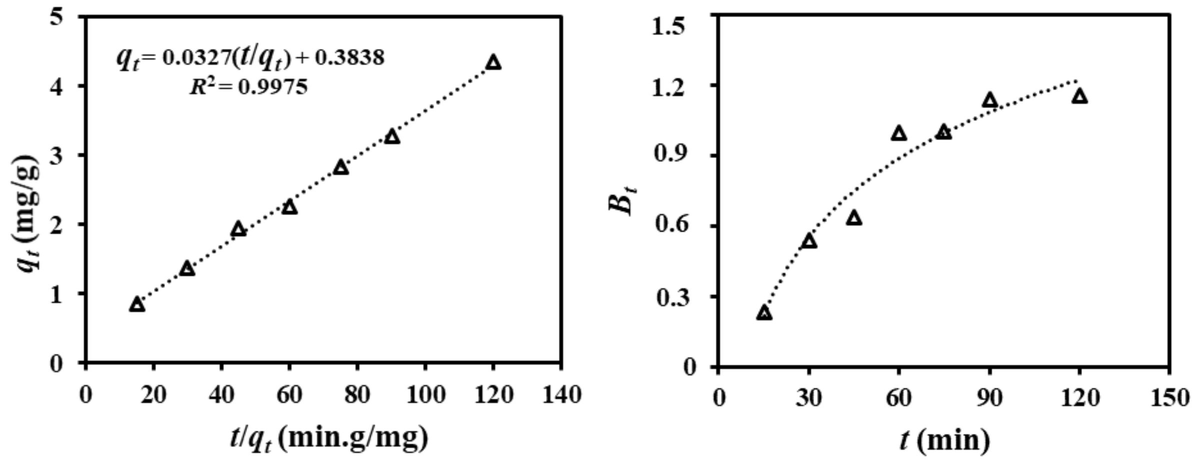

Fig. 5. (a). Pseudo-second order plot and (b). B_t vs t plot for adsorption of amoxicillin on ceria nanocrystal

Furthermore, the adsorption behaviour of amoxicillin on ceria nanocrystal was analysed to identify the embroiled mechanism in adsorption process. Two possible mechanisms that affect the rate-controlling adsorption process of amoxicillin on ceria nanocrystal are film and particle diffusion. The adsorption diffusion model applied to recognize whether film diffusion or particle diffusion that controlled adsorption rate [18].

$$B_t = -\ln(1 - F) - 0.4799 \qquad (7)$$

$$F = \frac{q_t}{q_e} \qquad (8)$$

Here, parameter F represents the fractional attainment of equilibrium at time t. The value of B_t was calculated for each F value using Eq.7. Fig. 5(b) shows the plot of B_t vs t for adsoprtion of amoxicillin on ceria nanocrystal. In the case B_t vs t plot is linear and passes through the origin, the adsorption process is dominated by particle diffusion. If the B_t vs t plot is non-linear, the adsorption process is controlled by film diffusion [18]. As can be seen in Fig. 5(b) the obtained B_t vs t plot is non-linear indicating that rate-controlling process is film diffusion.

Summary

This study investigated the adsorption properties of ceria nanocrystal which feasible to be applied for amoxicillin removal from water. The results reveal that the adsorption of amoxicillin on ceria nanocrystal well described by Langmuir isotherm with maximum adsorption capacity of 37.18 mg/g. The adsorption kinetic of amoxicillin on ceria nanocrystal, which controlled by film diffusion, corresponds to the pseudo second order kinetic model. The high removal efficiency of amoxicillin obtained for ceria nanocrystal dosage of 15 mg at temperature range 303-323K. However, further research is required to determine other adsorption parameters, such as pH so that a higher efficiency obtained.

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