Journal of Engineering Science and Technology
Vol. 17, No. 5 (2022) 3203 - 3210

ISOTHERM ADSORPTION CHARACTERISTICS OF 63-UM CALCIUM CARBONATE PARTICLES PREPARED FROM EGGSHELLS WASTE

ASEP BAYU DANI NANDIYANTO*,
GABRIELA CHELVINA SANTIULY GIRSANG, REFIKA SAFITRI RIZKIA

Universitas Pendidikan Indonesia, Jl. Dr. Setiabudhi No. 299, Bandung, 40154, Indonesia
*Corresponding Author: nandiyanto@upi.edu

Abstract

The study aimed to evaluate the isotherm adsorption characteristics of calcium carbonate particles prepared from eggshells using isotherm adsorption models (Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, and Hill-de Boer). The calcium carbonate particles were prepared by cleaning, drying, mashing, and carbonizing eggshells (250 °C; 2 hours). The adsorption test was conducted by evaluating curcumin solution adsorption using prepared calcium carbonate (63 μm) at the ambient condition with constant pressure, neutral pH, and room temperature (25 °C). The most suitable model to represent the adsorption phenomenon were sequentially Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, and Hill-de Boer. The results showed that 63-μm sized calcium carbonate particles have micropores with multilayer adsorption profile, followed by physical adsorption with repulsion interaction between adsorbed molecules and uniform distribution of binding energies. This study informed the isotherm properties evaluation of calcium carbonate from household/food processing waste, namely eggshells, as a potentially inexpensive and abundant adsorbent source.

Keywords: Calcium carbonate, Eggshell waste, Isotherm adsorption, Isotherm model, Microparticles.

1. Introduction

The vast amount of domestic and food processing waste generated around the world continues to be a major environmental concern. One of them is eggshells. Several reports have found that such biomass waste can be converted into calcium carbonate [1]. Eggshells contain a lot of carbon, roughly 30% of their weight, followed by 50% oxygen, 12.48% calcium carbonate, and 7.5% other inorganic elements [2]. Thus, eggshells were an inexpensive, abundant, and excellent calcium carbonate material.

The isotherm adsorption model can be used to predict, compare, and offer information such as the adsorption mechanism, the adsorption capacity, and the adsorption process [3]. Isotherm adsorption revealed important details on the mechanism, capacity, adsorption parameters, and design optimization [4]. The adsorption process and interaction between adsorbent and adsorbate were characterized by the adsorption isotherm factor. Therefore, this study aimed to evaluate the isotherm adsorption characteristic of prepared calcium carbonate from eggshells waste by using isotherm models.

This study focused to analyse the isotherm adsorption of calcium carbonate from eggshells waste. Such waste was the main focus as the calcium carbonate source due to its high calcium carbonate content, making them a prospective calcium carbonate raw material. Other novelties were the evaluation of isotherm adsorption in the micrometer range. The results were compared with several standard isotherm adsorption models (i.e. Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, and Hill-Deboer). Micrometer-sized particles are interesting to study because they settle and decant spontaneously, unlike nanoparticles that require specific treatments for the separation process. The microparticles benefit from their settling capacity since it prevents contamination during the analysis, allowing for more exact evaluation. Curcumin was chosen as the adsorbate model because it has an optimum molecular size (less than 1,4 nm), making it excellent for analysing adsorbent-adsorbate interactions and predicting various adsorption phenomena [5].

In this study, the calcium carbonate particles were prepared by carbonizing eggshells waste (250 °C; 2 hours) and sieved them into 63 μm-size. The adsorption test was carried out by using curcumin as the adsorbate model. There were four isotherm adsorption models used in this study: Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, and Hill-de Boer. This study informed the evaluation of calcium carbonate particles from household/food processing waste, specifically eggshells, as a potentially inexpensive and abundant adsorbent source.

1.1. Temkin isotherm model

Temkin model defined a factor that specifically refers to the interaction between adsorbent adsorbate. According to the model, the heat of adsorption of all molecules in the layer is a function of temperature [6]. The Temkin model was expressed in Eq. (1).

$$q_e = \beta_T (\ln C_e) + (\beta_T \ln A_T) \quad (1)$$

where q_e is the number of molecules adsorbed per gram at equilibrium (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), and A_T is the equilibrium binding constant. β_T is the Temkin's isotherm constant, where:

(i) $\beta_T < 8$ kJ implies physisorption

(ii) $\beta_T > 8$ kJ implies chemisorption

1.2. Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich model described the adsorption mechanism on a heterogeneous surface with Gaussian energy [7], expressed by Eq. (2).

$$\ln q_e = \ln q_s - \beta\varepsilon^2 \quad (2)$$

where q_s is the saturation capacity of theoretical isotherm (mg/g), β is the Dubinin-Radushkevich's isotherm constant related to the average free adsorption energy per mol of adsorbate, C_e is the equilibrium constant and ε is the Polanyi potential during the equilibrium condition (Eq. (3)). The type of adsorption can be predicted by the energy (E; kJ/mol) calculated with Eq. (4), where E < 8 kJ/ mol implies physical adsorption and E > 8 kJ/mol implies chemical adsorption.

$$\varepsilon = RT\ ln\ \left[1 + \frac{1}{C_e}\right] \quad (3)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (4)$$

1.3. Fowler-Guggenheim isotherm model

The Fowler-Guggenheim model described adsorbate's lateral interaction with weak Van der Waals interaction between adsorbed molecules at adjacent sites [8]. The model is expressed in Eq. (5).

$$\ln\left(\frac{C_e(1-\theta)}{\theta}\right) - \frac{\theta}{1-\theta} = -\ln K_{FG} + \frac{2W\theta}{RT} \quad (5)$$

where K_{FG} is the Fowler-Guggenheim's constant, W is the adsorbed adsorbate at the active site (replying to the interaction of adsorbate-adsorbent), and W is the interaction energy between two adsorbate molecules at the adjacent neighboring site (kJ/mol) where:

(i) W > 0 kJ/mol implies attractive interaction

(ii) W < 0 kJ/mol implies repulsive interaction

(iii) W = 0 kJ/mol implies no interaction

1.4. Hill-Deboer isotherm model

Hill-Deboer model defined bilateral interaction and mobile adsorption between adsorbed molecules [9], expressed in Eq. (6).

$$\ln\left(\frac{C_e(1-\theta)}{\theta}\right) - \frac{\theta}{1-\theta} = -\ln K_1 + \frac{K_2\theta}{RT} \quad (6)$$

where K_1 is the Hill-Deboer constant (L/mg), and K_2 is the energetic constant of the interactions between adsorbed molecules (kJ/mol). K_2 can imply attraction or repulsion between molecules with conditions as follows:

(i) K_2 > 0 kJ/mol implies attraction between adsorbed molecules

(ii) K_2 < 0 kJ/mol implies repulsion between adsorbed molecules

(iii) K_2 = 0 kJ/mol implies no attraction between adsorbed molecules

2. Method

Eggshells and turmeric were purchased from local markets in Bandung, Indonesia. Eggshells were cleaned, dried, mashed, and carbonized in an electrical furnace

(SHARP; Model EO-28LP(K), China) for 2 hours (250 °C). After that, the calcium carbonate particles were saw-milled (Miyako; BL-102 PL) and put into sieving apparatus (PT. Rumah Publikasi Indonesia) to get 63 μm-sized particles. To investigate the adsorption characteristics, curcumin was used as an adsorbate model [6, 10-12]. Curcumin solution was made by dissolving turmeric powder in water. The adsorption test was carried out by adding 0.10 g calcium carbonate particles to 100 mL of curcumin solution with a specific concentration (10, 30, 50, 70, and 90 ppm) [13]. The solution was then mixed for 1 minute. After 30 minutes, the concentration change of curcumin solution was measured using a TDS meter (TDS&EC; Model E-1 Portable). The experiment was carried out by avoiding sunlight since the curcumin solution is sensitive to photoreaction and oxidation. Furthermore, the model fitting and analysis were performed using Microsoft Excel.

3. Results and Discussion

The best fit or suitable model to depict the adsorption process was determined using the linear regression value (R^2). Subsequently, the best-fit isotherm models were Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, and Hill-Deboer. The parameter of those models was calculated to study the adsorption process and shown in Table 1.

The result showed that the Temkin model was the most appropriate model for representing the calcium carbonate microparticles' adsorption behavior (Fig. 1(a)). The Temkin's isotherm constant (B_T) was found less than 8 kJ/mol. It means that the adsorption followed a physical process where weak van der Waals are associated between adsorbate and adsorbent. Although physisorption has low uptake, it has quick adsorbing and desorbing speed, excellent reversibility, and high cycling stability. This type of adsorption can ensure that only a small amount of energy was needed for regeneration [14]. The binding energies were uniformly distributed during the adsorption process (since the R^2 value in the Temkin model was higher than 0.70). The characterization of uniform distribution of binding energy affected the linear decreases of the heat adsorption rather than logarithmically for all molecules in the layer [12].

According to the E value in the Dubinin-Raduskevich model (Fig. 1(b)), physical interaction of adsorbate-adsorbent was taken place (confirmed by B_T value from Temkin model). This model also implied the existence of micropores on the adsorbent surface. Pore sizes smaller than 12 μm were considered micropores [15]. The formation of micropores (12 μm) was expected since we used 63-μm calcium carbonate particles, which are already small. The micropores can increase the surface area needed for adsorption.

Figure 1(c) shows the linear fitting of the Fowler-Guggenheim model. The W value was lower than 0 kJ/mol, indicating that there was repulsion attraction between adsorbed molecules. The repulsion interaction happened between surface-adsorbed molecules and dissolved adsorbate [16]. Adjacent adsorbed molecules exerted a repulsive force on the adsorbate molecules [17, 18] that approaching the surface of the calcium carbonate. The adsorption process was following an endothermic reaction. On the other hand, as the third most suitable model, the linear fitting of Fowler-Guggenheim implied that the adsorbent's surface has a multilayer characteristic.

According to the Hill-Deboer model (Fig. 1(d)), the K_2 was found lower than 0 kJ/mol, indicating that there was a repulsion interaction between adsorbed molecules. In addition, the R^2 value, which was higher than 0.70, showed a multilayer surface adsorption occurring on the adsorbent surface. Both results were confirmed by the Fowler-Guggenheim model. Although the linear regression value of the Hill-Deboer was 0.9018, this model was the least suitable for describing the adsorption process.

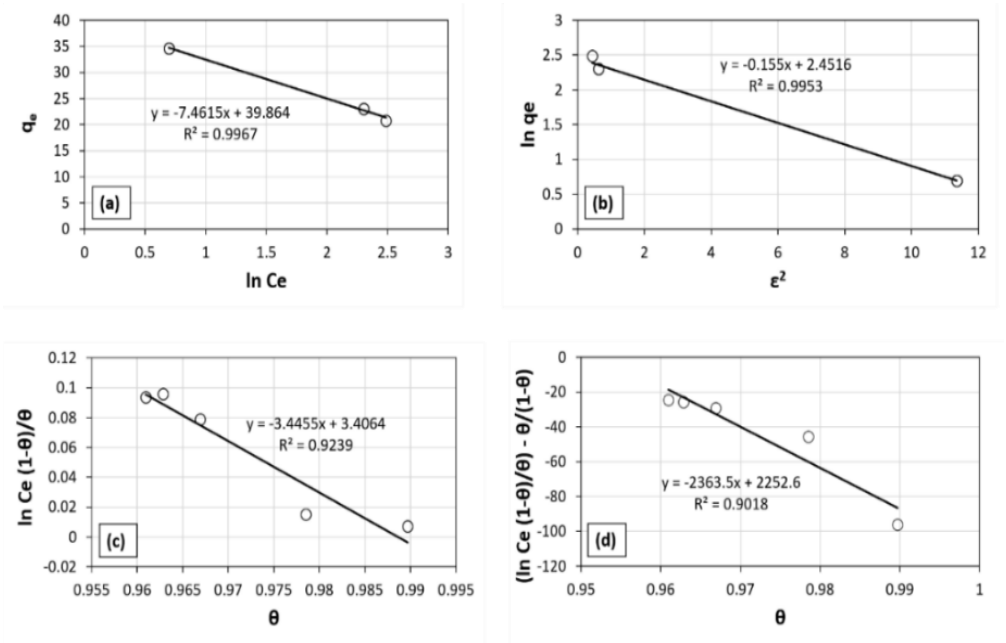

Fig. 1. Linear fitting of Temkin (a), Dubinin-Radushkevich (b), Fowler-Guggeinheim (c), and Hill-Deboer model (d).

The overall evaluation of isotherm models (Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, and Hill-Deboer) was significant to understand the occurring adsorption phenomenon, illustrated in Fig. 2.

Our previous reports have studied the adsorption mechanism of curcumin by using carbon prepared from pineapple peels, silica from rice husks, and calcium carbonate from fish bones [13]. The adsorption profiles of carbon prepared from pineapple peels showed Freundlich multilayer and cooperative adsorption with a physical process [12]. On the other hand, silica microparticles prepared from rice husks followed the Freundlich isotherm model, where the adsorption occurred on a heterogeneous surface with multilayer adsorption [6].

In comparison, the adsorption mechanism reported in this study was similar to the findings of our previous report [13, 14]. The calcium carbonate from fishbone followed multilayer adsorption with physical and endothermic processes, similar to this study's findings. However, different from this report where the adsorption profile followed the Temkin model, the calcium carbonate prepared from fishbone was most suited with the Hill-de Boer model. This could be due to the different raw materials and methods used to produce calcium carbonate.

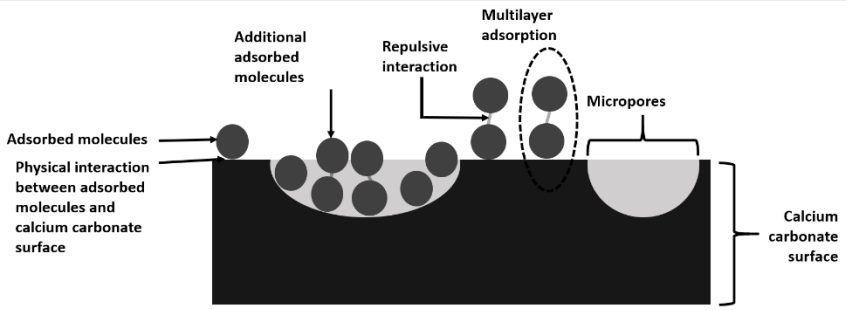

Fig. 2. Adsorption profile illustration of the prepared calcium carbonate.

Table 1. Isotherm adsorption parameter value and description.

Model	Parameter	Value	Notes
Temkin	A_T (L/g)	0.005	The equilibrium constant
	B_T (J/mol)	-332.067	B_T < 8 kJ/mol, there is physical interaction between adsorbate and adsorbent
	R^2	0.9967	R^2 > 0.70, there is the uniform distribution of binding energies between adsorbate and the adsorbent surface
Dubinin-Radushkevich	$\beta\ \left(\mathrm{mol}^2/\mathrm{kJ}^2\right)$	0.155	The Dubinin-Radushkevich constant
	$E\left(\mathrm{kJ}/\mathrm{mol}\right)$	1.796	E < 8 kJ/mol, there is physical interaction between adsorbate molecules
	R^2	0.9953	R^2 > 0.70, there are micropores in the adsorbent surface
Fowler-Guggenheim	K_{FG}(L/mg)	1.576×10^{-15}	The Fowler-Guggenheim constant
	W(kJ/mol)	-138488.912	W < 0 kJ/mol, there is repulsion interaction between adsorbed molecules; endothermic process
	R^2	0.9239	R^2 > 0,70, the surface of the adsorbent was multilayer
Hill-Deboer	K_1(L/mg)	0	The Hill-Deboer constant
	K_2(kJ/mol)	-6042329.780	K_2 < 0 kJ/mol, there is repulsion interaction between adsorbed molecules
	R^2	0.9018	R^2 > 0,70, the surface of the adsorbent was multilayer

4. Conclusion

Isotherm adsorption characteristics (obtained using Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, and Hill-de Boer model) of calcium carbonate microparticles prepared from eggshells waste were investigated. The best isotherm model that fits the results was Temkin. The results showed that 63-μm sized calcium carbonate particles had micropores and were following physical adsorption with repulsion interaction between adsorbed molecules. The adsorption process has a uniform distribution of adsorbate-adsorbent surfaces with multilayer adsorption.

Acknowledgements

We acknowledged RISTEK BRIN, Grant Penelitian Terapan Unggulan Perguruan Tinggi and Bangdos, Universitas Pendidikan Indonesia.

References

1. Yahya, M.A.; Al-Qodah, Z.; and Ngah, C.Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. *Renewable and Sustainable Energy Reviews*, 46(2015), 218-235.
2. Habeeb, O.A.; Ramesh, K.; Ali, G.A.M.; and Yunus, R.M. (2017). Isothermal modelling based experimental study of dissolved hydrogen sulfide adsorption from waste water using eggshell based activated carbon. *Malaysian Journal of Analytical Sciences*, 21(2), 334-345.
3. Ragadhita, R.; and Nandiyanto, A.B.D. (2021). How to calculate adsorption isotherms of particles using two-parameter monolayer adsorption models and equations. *Indonesian Journal of Science and Technology*, 6(1), 205-234
4. Chen, X. (2015). Modeling of experimental adsorption isotherm data. *Information*, 6(1), 14-22.
5. Nandiyanto, A.B.D.; Sofiani, D.; Permatasari, N.; Sucahya, T.N.; Wiryani, A.S.; Purnamasari, A.; Rusli, A.; and Prima, E.C. (2016). Photodecomposition profile of organic material during the partial solar eclipse of 9 March 2016 and its correlation with organic material concentration and photocatalyst amount. *Indonesian Journal of Science and Technology*, 1(2), 132-155.
6. Ragadhita, R.; Nandiyanto, A.B.D.; Nugraha, W.C.; and Mudzakir, A. (2019). Adsorption isotherm of mesopore-free submicron silica particles from rice husk. *Journal of Engineering Science and Technology*, 14(4), 2052-2062.
7. Mohammadnia, E.; Hadavifar, M; and Veisi, H. (2019). Kinetics and thermodynamics of mercury adsorption onto thiolated graphene oxide nanoparticles. *Polyhedron*, 173(2019), 114139.
8. Nandiyanto, A.B.D.; Maryanti, R.; Fiandini, M.; Ragadhita, R.; Usdiyana, D.; Anggraeni, S.; Arwa, W.R.; and Al-Obaidi, A.S.M. (2020). Synthesis of carbon microparticles from red dragon fruit (Hylocereus undatus) peel waste and their adsorption isotherm Characteristics. *Molekul*, 15(3), 199-209.
9. Ragadhita, R.; and Nandiyanto, A.B.D. (2021). How to calculate adsorption isotherms of particles using two-parameter monolayer adsorption models and equations. Indonesian *Journal of Science and Technology*, 6(1), 205-234.

10. Nandiyanto, A.B.D. (2020). Isotherm adsorption of carbon microparticles prepared from pumpkin (Cucurbita maxima) seeds using two-parameter monolayer adsorption models and equations. *Moroccan Journal of Chemistry*, 8(3), 8-3.
11. Nandiyanto, A.B.D.; Arinalhaq, Z.F.; Rahmadianti, S.; Dewi, M.W.; Rizky, Y.P.C.; Maulidina, A.; Anggraeni, S.; Bilad, M.R.; and Yunas, J. (2020). Curcumin adsorption on carbon microparticles: synthesis from soursop (AnnonaMuricata L.) peel waste, adsorption isotherms and thermodynamic and adsorption mechanism. *International Journal of Nanoelectronics and Materials*, 13(2020), 173-192.
12. Nandiyanto, A.B.D.; Girsang, G.C.S.; Maryanti, R.; Ragadhita, R.; Anggraeni, S.; Fauzi, F.M.; and Al-Obaidi, A.S.M. (2020). Isotherm adsorption characteristics of carbon microparticles prepared from pineapple peel waste. *Communications in Science and Technology*, 5(1), 31-39.
13. Nandiyanto, A.B D.; Erlangga, T.M.S.; Mufidah, G.; Anggraeni, S.; Roil, B.; and Jumril, Y. (2020). Adsorption isotherm characteristics of calcium carbonate microparticles obtained from barred fish (Scomberomorus spp.) bone using two-parameter multilayer adsorption models. Mechanism. *International Journal of Nanoelectronics & Materials*, 13(2020), 45-58.
14. Karanikolos, G.N.; Romanos, G.E.; and Vega, L.F. (2021). Chemical modification of adsorbents for enhanced carbon capture performance. *Frontiers in Chemistry*, 9(2021), 667669.
15. Guo, C.; and Cui, Y. (2020). Pore structure characteristics of debris flow source material in the Wenchuan earthquake area. *Engineering Geology*, 267(2020), 105499.
16. Sun, C.; Xiong, B.; Pan, Y.; and Cui, H. (2017). Adsorption removal of tannic acid from aqueous solution by polyaniline: analysis of operating parameters and mechanism. *Journal of colloid and interface science*, 487(2017), 175-181.
17. Ituen, E.; Akaranta, O.; and James, A. (2017). Evaluation of performance of corrosion inhibitors using adsorption isotherm models: an overview. *Chemical Science International Journal*, 18(1), 1-34.
18. Zhou, M.; and Liu, B. (2017). First-principles investigation of adsorbate–adsorbate interactions on Ni (111), Ni (211), and Ni (100) surfaces. *Industrial and Engineering Chemistry Research*, 56(20), 5813-5820.