Moroccan Journal of Chemistry
ISSN : 2351-812X

Mor. J. Chem., 2024, Volume 12, Issue 3, Page 1073-1096
https://revues.imist.ma/index.php/morjchem
https://doi.org/10.48317/IMIST.PRSM/morjchem-v12i3.48106

Characteristics of Ammonia Adsorption on Various Sizes of Calcium Carbonate Microparticles from Chicken Eggshell Waste

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Received *12 Mar 2024,*
Revised *29 Apr 2024,*
Accepted *1 May 2024*

Citation*: Nandiyanto A.B.D., Putri M. E., Fiandini M., Ragadhita R., Kurniawan T., Farobie O., Bilad M. R. (2024) Characteristics of Ammonia Adsorption on Various Sizes of Calcium Carbonate Microparticles from Chicken Eggshell Waste, Mor. J. Chem., 12(3), 1073-1096*

Abstract: The purpose of this study was to synthesize calcium carbonate from chicken eggshell waste for ammonia adsorption. Experiments were done by heating eggshell waste. The heated materials were then milled and sieved to get calcium carbonate microparticles with a specific size (500, 1000, and 2000 μm). The particles were then characterized using a microscope and infrared spectroscopy (FTIR) to identify particle morphology and functional groups, respectively. The prepared particles were then used for ammonia adsorption, tested, and compared with ten isotherm models (such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Jovanovic, Halseys, Harkin-Jura, Flory-Huggins, Fowler-Guggenheim, and Hill-Deboer) to identify the adsorption mechanism. The pseudo-second-order kinetic model was suggested for describing the adsorption process that occurs to form a complex multilayer layer between the adsorbent and the adsorbate. This result was supported by the investigation of the adsorption isotherm model, which found that all particle sizes have a pattern where a multilayer layer is formed due to the distribution of pores. Layer formation during the adsorption process involves physisorption and chemisorption with spontaneous and endothermic systems. The particle size confirms the difference in ability as indicated by the adsorption capacity value. The smaller the particle size, the greater the maximum capacity because it has a large surface area. On the other hand, the smaller particle size impacts the obtainment of the greater maximum capacity because of its large surface area. This study shows that the use of eggshell waste has the potential. This study shows that the use of eggshell waste has the potential to be used as an adsorbent and supports the Sustainable Development Goals (SDGs) program.

Keywords: *Adsorption; Adsorbent; Ammonia; Calcium carbonate; Chicken eggshell waste*

1. Introduction

Water contamination is a major concern worldwide due to its serious impact on human health, ecosystems, and economies (Sharma and Bhattacharya, 2017). Sources of contamination water can come from industrial activities, dyes, metals, pesticides, fertilizers, radioactivity, etc (Mishra *et al.*, 2023; Akartasse *et al.*, 2017; Brahimi *et al.*, 2015; Lamhamdi *et al.*, 2014;). One source that greatly

contributes to water pollution is the activity of the fertilizer industry which produces ammonia waste (Det *et al*., 2021; Khan *et al*., 2020; Fathi *et al*., 2021) Ammonia waste is a type of waste that contains ammonia compounds in high concentrations. Ammonia (NH_3) or ammonium (NH_4) in high concentrations has a major impact on the environment such as the eutrophication process in water bodies, reducing dissolved oxygen levels, inhibiting the decomposition of organic substances through microorganisms (excessive ammonia concentration). In addition, water contaminated with ammonia can cause serious health problems in humans such as infectious, respiratory, and skin diseases.

To overcome water contamination due to ammonia, the development and implementation of water treatment such as filtration (Cescon and Jiang, 2020), coagulation (Bahrodin *et al*., 2021), flocculation (Teh *et al*., 2016), and advanced oxidation (Rekhate and Srivastava, 2020) have a crucial role in ensuring the water is clean and safe for use. However, the application of this method has the main disadvantage of high operational costs, especially for advanced oxidation which requires special equipment and additional chemicals. In addition, coagulation and reflex methods produce chemical residues that require further steps to remove them (Miklos *et al*., 2018; Khaneghah *et al*., 2022). Filtration methods cannot completely remove small or highly soluble contaminants in the water. Meanwhile, the oxidation process takes longer and requires strict compliance to ensure optimal processing efficiency. Because this method has shortcomings that cause water processing to be inefficient, other methods are needed. Adsorption offers many advantages over other methods such as filtration, coagulation, flocculation, and advanced oxidation (Ragadhita *et al*., 2023; Ad *et al*., 2016). One of the advantages of the adsorption method is that it can remove certain contaminants from the solution, thereby producing clean water with high clarity (Crini *et al*., 2019). Apart from being efficient, the adsorption process is also relatively easy to carry out and requires simpler equipment than other methods. In addition, adsorption can also be combined with other technologies or used in modular systems that can be adapted to the specific needs of the location and air source (Nandiyanto *et al*., 2023a; Nandiyanto *et al*., 2023b; Ragadhita *et al*., 2023). Over the last few years, many researchers have successfully carried out adsorption research using various wastes from agriculture, fishery, and livestock as adsorbents, which are presented in **Table 1**.

However, in **Table 1**, the successful adsorption using adsorbents from various sources (such as agricultural, livestock, and fishery waste) has been explained in removing various contaminants. Nevertheless, there is still little research regarding the treatment of water contaminated with ammonia, especially using eggshell waste. Eggshells are widely used as adsorbents because they are easy to find and cheap. Additionally, eggshell waste also contains 98.5% $CaCO_3$, 0.85% $MgCO_3$, and 0.02 g of phosphorus with a small amount of iron and sulfur. This content contains carbon and oxygen elements which are an alternative to eggshells for use as an adsorbent (Mittal *et al*., 2016). Apart from that, the bibliometric results provide an overview of the development of eggshell research which continues to increase every year which can be seen in **Figure 1**. This confirms that eggshells attract the attention of researchers to use eggshells as a promising adsorbent. The use of bibliometrics has been widely used because it makes it easier to understand research trends from year to year. **Table 2** displays comprehensive research on bibliometrics. This bibliometric study has been well-documented, and can be found in recent literature published in 2023-2024 (Utama *et al.*, 2023; Sahidin, *et al.*, 2023; Hamidah *et al.*, 2023; Arianingrum *et al.*, 2023; Rahmat *et al.*, 2023; Abduh *et al.*, 2023; Mardina *et al.*, 2024; Solihah *et al.*, 2024; Yang *et al.*, 2024; Angraini *et al.*, 2024; Nurramadhani *et al.*, 2024; Imaniyati *et al.*, 2024; Amida *et al.*, 2024; Kadir *et al.*, 2024; Shidiq, 2023; Nandiyanto *et al.*, 2024; Lizama *et al.*, 2024; Al Husaeni *et al.*, 2024a; Al Husaeni *et al.*, 2024b; Laita *et al.*, 2024).

Table 1. Previous studies on adsorption used adsorbents based on livestock, fishery, and agricultural waste

No	Raw Material	Type of adsorbent	Type of contaminant removed	Results	Ref.
1	Soybean dreg	Carbon porous	Deoxynivalenol	Porous carbon is very good in removing deoxynivalenol because it has a high specific surface area and many effective functional groups	(Ying *et al.*, 2021)
2	Coconut dregs	Carbon activated	Cu (II), Ni (II) and Pb (II) ion	The more complexity of the metal ion affects the adsorption ability. Langmuir model shows suitability during the adsorption process	(Kamari *et al.*, 2014)
3	Sawdust	Carbon	Methylene blue method	The concentration of urea as an activation agent affects the adsorption ability. The higher the urea concentration, the greater the adsorption capacity of methylene blue.	(Ortega-Toro et al., 2023)
4	Pomelo peel	Carbon	Hexavalent chromium (Cr(VI))	Carbon modification with $FeCl_3$ shows better performance than without modification. This indicates that it is more efficient to use modified pomelo-based carbon.	(Wang *et al.*, 2020)
5	Rice husk	Carbon porous	Curcumin dyes	Carbon fabrication from rice husks has an agglomerated porous structure. The adsorption isotherm follows the Freundlich model with multilayer characteristics.	(Fiandini *et al.*, 2020)
6	Mangosteen Peel	Carbon	Curcumin dyes	Particle size affects the ability of the adsorption process. For large particles, the adsorption process occurs in multilayers with a porous surface. Meanwhile, small-sized particles occur in a monolayer with a porous surface.	(Nandiyanto *et al.*, 2023a)
7	Eggshell	$CaCO_3$	Ion Ni^{2+}	The adsorption process follows pseudo-first-order kinetics. Additionally, the Langmuir fitted adsorption model was compared with the Freundlich, Temkin, and Dubinin-Raduskevic isotherm models.	(De Angelis *et al.*, 2017)
8	Oyster shells	$CaCO_3$	Ion Flouride	Exothermic reactions that benefit the adsorption process. In addition, the adsorption kinetics follow pseudo-second-order. The isotherm properties follow the Langmuir model with Q_{max} 27.31 mg/g.	(Hashemkhani *et al.*, 2022)
9	Crab shell	$CaCO_3$	Cargo dye red	The adsorption mechanism follows Langmuir with an adsorption capacity of 20,317 mg/g. Interactions between particles are based on electrostatics, hydrogen bonds, and π-π interactions.	(Dai *et al.*, 2018)
10	Fishbone	$CaCO_3$	Curcumin dyes	The size of adsorbents affects the increase in adsorbent capacity. The adsorption mechanism is multilater and best fits the Hill-de Boer model.	(Nandiyanto *et al.*, 2020)

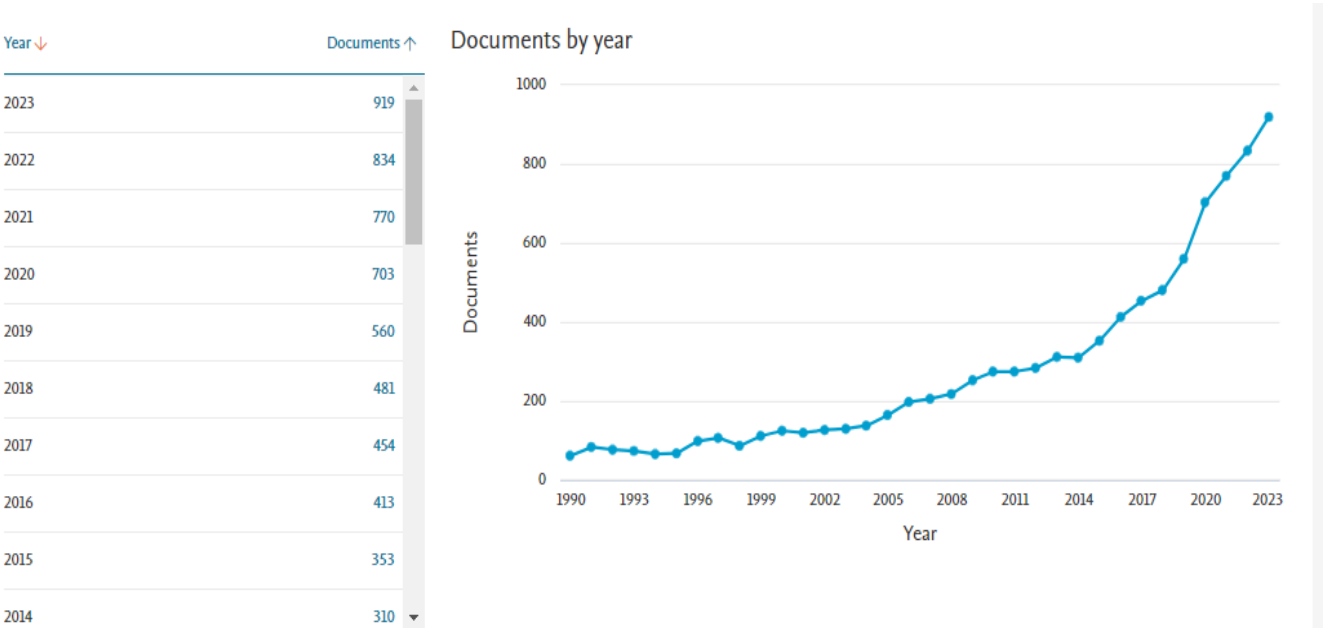

Figure 1. Publication results of "eggshell" and "adsorption". Data was obtained from Scopus taken in February 2024. Detailed information on how to use bibliometrics is presented elsewhere (Al Husaeni and Nandiyanto, 2022).

Here, the purpose of this study was to synthesize calcium carbonate from chicken eggshell waste for ammonia adsorption. We also focused on understanding isotherm adsorption and investigating phenomena happening during the adsorption. This study also considers the size of the adsorbent (i.e. 500, 1000, and 2000 μm sizes) to confirm the evaluation of the phenomena. Indeed, it has been well-known that the size of the adsorbent affects the available surface area, pore accessibility, and adsorption speed; thus, it prmoting the change in the the adsorption capability and efficiency of the water treatment (Iwuozor *et al*., 2021).

To support the understanding in the phenomena happening during adsorption, this study explores the calculation using ten isotherm adsorption models, including Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Jovanovic, Halsey, Harkin Jura, Flory-Huggins, Fowler-Guggenheim, and Hill-DeBoer. This study is expected to help understand the adsorption mechanisms involved in designing and optimizing adsorption processes more efficiently and predicting the adsorption behavior of certain substances on certain adsorbent surfaces. Here, in this study, we also provide bibliometric analysis to identify research trends in determining future research directions about eggshells as adsorbents in the adsorption process.

Among these materials, utilizing eggshell waste-based adsorbents stands out several advantages: (i) low cost due to the use of waste-based adsorbents that are abundant and cheap; (ii) environmentally friendly because the adsorbents that have been used can be biologically degraded and do not cause new pollutants in the adsorption process; and (iii) the adsorption process using eggshell waste is relatively easy to apply on a small and large scale without the need for complex equipment. In addition, the adsorption process utilizing eggshell waste-based adsorbents, in practice, helps reduce waste problems, as we reported in our previous studies. Also, this study presents novelty in the field of waste management and sustainable adsorbent material development such as (i) the use of eggshell waste, providing knowledge on new ways of managing and utilizing waste;

Table 2. Previous studies on bibliometric

Topics Bibliometrics	Results	Reference
Adaptive learning trends using gamification	Using the VOSviewer, a bibliometric analysis of adaptive gamification revealed a surge in research in 2019 and 2020 and a decline in 2021.	(Hayati and Hirawan, 2023)
Development of research regarding biodiesel performance	A bibliometric review of 127 papers demonstrated the benefits of B100, a diesel engine fuel; nevertheless, more research on engine sizes, raw materials, and testing circumstances is required.	(Setiyo *et al*., 2021)
Understanding Chemistry in Special Needs Education.	Publish or Perish and VOSviewer were used to analyze articles on chemistry and special education. The results revealed a decrease in publications in 2017 and an increase in 2021.	(Bilad, 2022)
Teaching biotechnology in increasing the progress of education sustainable development	Teaching green chemistry in schools is important, as evidenced by the four study concept potentials that the bibliometric analysis of research trends on biotechnology in education found, with journals being the most common source.	(Riandi *et al*., 2022)
The development of engineering science in education	Pandemic conditions caused a considerable decline in education, science, and engineering research, according to a study that used the VOSviewer and Perish programs to evaluate these areas.	(Nordin, 2022)
Teaching chemical engineering in special education schools	The association between chemical engineering and special needs was the subject of a research study that looked at 800 relevant papers between 2018 and 2022 using the VOSviewer program.	(Wirzal and Putra, 2022)
Development of briquette research during the Covid-19 pandemic.	The COVID-19 epidemic has resulted in a decrease in research over the past three years, according to an examination of 973 relevant papers on briquettes conducted using VOSviewer, bibliometric analysis, and data mapping.	(Al Husaeni, 2022)
Teaching mathematics education in constructivist and computational thinking	Using bibliometric analysis, the study examined the rise in constructionism, constructivism, computational thinking, and mathematics education articles to find prolific authors and academics who are frequently cited.	(Supriyadi et al., 2022)
Learning about water hyacinth at school	Research on the use of water hyacinth water as a source and learning medium is relatively uncommon, according to a study of the literature. Nonetheless, there is still some water hyacinth research being conducted in Indonesia's educational system. Among those utilized in early childhood education, elementary school, and middle school are water hyacinths as a source and teaching tool.	(Fiandini *et al*., 2023)
Magnetic production of Fe_3O_4 nanoparticles	The findings indicate that there was a rise in Fe_3O_4 nanoparticle production between 2017 and 2019 followed by a decline. It is anticipated that this study will assist and serve as a resource for future researchers when choosing the research topic to pursue.	(Nugraha and Nandiyanto, 2022)
Geothenics fields as branch science	Bibliometric maps with network, overlay, and density visualizations for keyword analysis purposes. "Displacement", "Strength", "Stress", and "Earthquake" are four terms that come up frequently.	(Mulyawati and Ramadhan, 2021)

(ii) the effect of adsorbent sizes in the adsorption, which can provide deep insight into what phenomena and how particle size can affect the adsorption process; and (iii) the focus on ammonia as the model adsorbate provides direct implications for water treatment efforts. This study concluded that the eggshell waste is prospective to be used as an environmentally friendly adsorbent for ammonia removal applications from wastewater, offering a sustainable and effective alternative adsorbent to existing water treatment technologies and solving current issues in the sustainable development goals (SDGs), while SDGs now is taught to society (Nurramadhani *et al.*, 2024; Makinde *et al.*, 2024; Gemil *et al.*, 2024; Haq *et al.*, 2024; Basnur *et al.*, 2024; Maulana *et al.*, 2023; Nurnabila *et al.*, 2023; Awalussillmi *et al.*, 2023; Rahmah *et al.*, 2024; Keisyafa *et al.*, 2024).

2. Basic Theory

2.1. Theory of Isotherm Adsorption Model

This study uses mathematical equations of ten adsorption isotherm models. The adsorption isotherm model predicts the adsorption behavior of a substance on the adsorbent surface more accurately. In addition, by fitting the experimental data with an appropriate isotherm model, important parameters such as maximum adsorption capacity, adsorption constant, and adsorption energy can be evaluated. For a complete understanding, previous literature provides detailed calculations of the adsorption isotherm (Ragadhita and Nandiyanto *et al.*, 2021).

2.1.1 Langmuir Model

This model is based on the fact that each adsorption site contains only one molecule with the same and equivalent identical number that occurs at a homogeneous location site and cannot interact with each other. The Langmuir calculation formula can be expressed in **Eqn. 1**:

$$\frac{1}{qe} = \frac{1}{qmax^{Kl}}\frac{1}{C_e} + \frac{1}{qmax} \qquad \textbf{Eqn. 1}$$

In the Langmuir equation, q_{max} is the Langmuir equilibrium constant, indicating the maximum monolayer capacity in (mg/g). q_e is the number of molecules adsorbed at equilibrium (mg/g). The term K_L is the Langmuir constant. R_L represents the adsorption behavior: $R_L > 1$ indicates unfavorable adsorption, $R_L = 1$ indicates linear adsorption which is influenced by the number and concentration of adsorbed molecules, $R_L = 0$ indicates adsorption that is too strong or irreversible, and $0 < R_L < 1$ indicates favorable adsorption or no desorption. The calculation of the R_L adsorption behavior factors is presented in **Eqn. 2**:

$$R_L = \frac{1}{1 + K_L C_e} \qquad \textbf{Eqn. 2}$$

2.1.2. Freundlich Model

This model characterizes a form of physical adsorption where adsorption occurs in many layers, and the bonds are weak, representing multilayer adsorption shown in **Eqn. 3**:

$$log\ Q_e = logk_f + \frac{1}{n} log\ log\ C_e \qquad \textbf{Eqn. 3}$$

In this case, C_e is the adsorbate concentration at equilibrium (mg/L) and k_f is the Freundlich constant, which calculates the adsorption capacity. The Freundlich isotherm also explains the degree of linearity (n) in the adsorption process and can be explained as follows: if n = 1 it means linear adsorption; if n < 1 indicates an adsorption process with chemical interactions; when n > 1, it indicates an adsorption process with physical interactions. Favorable adsorption processes are recognized when 0 < 1/n < 1, and cooperative adsorption processes occur when 1/n > 1.

2.1.3. Temkin Model

This model assesses the interaction between the adsorbent and the adsorbate, emphasizing the uniform dispersion of binding energy across the surface of the adsorbent. This relationship is expressed by **Eqn. 4**:

$$q_e = B_T ln A_T + B_T ln C_e \qquad \textbf{Eqn. 4}$$

where A_T represents the equilibrium constant. The Temkin constant, denoted by β_T, defines the physical (β_T < 8 kJ) or chemical (β_T > 8 kJ) adsorption processes.

2.1.4. Dubinin-Radushkevich Model

This model describes the interaction between adsorbent and adsorbate, with a porous surface and mechanisms for high and low concentrations, which is represented by **Eqn. 5**:

$$ln q_e = ln q_s - (\beta \varepsilon^2) \qquad \textbf{Eqn. 5}$$

Where the average free adsorption energy is represented by the Dubinin-Radushkevich constant (β), and the saturation capacity (qs) is expressed in mg/g. **Eqn. 6** and **7** relate the value of ε, the Polanyi potential linked to equilibrium circumstances, to the adsorption energy (E):

$$\varepsilon = RT ln\left[1 + \frac{1}{C_e}\right] \qquad \textbf{Eqn. 6}$$

$$E = \frac{1}{\sqrt{2\beta}} \qquad \textbf{Eqn. 7}$$

E is associated with either chemical (E > 8 kJ) or physical (E < 8 kJ) adsorption.

2.1.5. Jovanovic Model

This model postulates the absence of mechanical contact between the adsorbate and the adsorbent. The Jovanovic isotherm is shown by **Eqn. 8**:

$$ln Q_e = ln Q_{max} - K_j C_e \qquad \textbf{Eqn. 8}$$

where Q_e is the adsorbate concentration at equilibrium (mg/g), Q_{max} is the adsorbate's maximum absorption, and K_J is the Jovanovic constant.

2.1.6. Halsey Model

This model assesses the multilayer adsorption system at a considerable distance from the surface. The Halsey model, like the Freundlich model, applies to both multilayer adsorption and heterogeneous surfaces with non-uniformly distributed adsorption heat, as shown in **Eqn. 9**.

$$\boldsymbol{Q_e = \frac{1}{n_H} lnK_H - \left(\frac{1}{n_H}\right) lnC_e} \qquad \textbf{Eqn. 9}$$

Where K_H and n represent Halsey's constants.

2.1.7. Harkin Jura Model

This model explains the occurrence of adsorption on the adsorbent surface as multi-layered adsorption, which is caused by the heterogeneous distribution of adsorbent pores, as depicted in **Eqn. 10**:

$$\boldsymbol{\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \left(\frac{1}{A}\right) logC_e} \qquad \textbf{Eqn. 10}$$

where, B_{HJ} represents the adsorbent's specific surface area, while A_{HJ} represents the Harkin-Jura constant.

2.1.8. Flory-Huggins Model

This model represents the mechanism of spontaneous adsorption on a multilayer surface, described in **Eqn. 11**.

$$\boldsymbol{log\ \frac{\theta}{Ce} = log\ log\ K_{FH} + n\ log\ log\ (1-\theta)} \qquad \textbf{Eqn. 11}$$

Where $\boldsymbol{\theta = \left(1 - \frac{C_e}{C_o}\right)}$ is the extent of monolayer covering. The Flory-Huggins model's equilibrium constants, n_{FH} and K_{FH}, correlate with the Gibbs free energy ($\Delta G°$), as shown in **Eqn. 12**.

$$\boldsymbol{\Delta G° = -RT\ ln\ K_{FH}} \qquad \textbf{Eqn. 12}$$

When it is negative, the $\Delta G°$ can be used to characterize the spontaneous and temperature-dependent nature of the adsorption

2.1.9. Fowler-Guggenheim Model

This model characterizes the effect of interaction contacts between species adsorbed at adjacent positions, presented in **Eqn. 13**.

$$\boldsymbol{K_{FG}C_e = \frac{\theta}{1-\theta} exp\ (\frac{2.\theta.W}{RT})} \qquad \textbf{Eqn. 13}.$$

where the Fowler-Guggenheim constant (L/mg) is represented by K_{FG}. When describing processes under exothermic ($W > 0$), endothermic ($W < 0$ kJ/mol), or no contact between adsorbed molecules ($W = 0$ kJ/mol) conditions, W is the interaction energy between the adsorbed molecules (kJ/mol).

2.1.10. Hill-DeBoer Model

This model describes mobile adsorption and the reciprocal interaction between the adsorbed molecules which is expressed in **Eqn. 14**.

$$K_1.C_e = \frac{\theta}{1-\theta} exp\ (\frac{\theta}{1-\theta} - \frac{K_2\theta}{RT}) \qquad \textbf{Eqn. 14}$$

The contact energy constants for the adsorbed molecules are denoted by K_1 (L/mg) and K_2 (kJ/mol). These values indicate whether the process is exothermic with intermolecular adsorption ($K_2 > 0$), endothermic with repulsion ($K_2 < 0$), or there is no interaction between the adsorbates ($K_2 = 0$).

2.2. Adsorption Kinetics

Adsorption kinetics is the study of how molecules or particles are absorbed by the surface of an adsorbent. Adsorption is a process where molecules, atoms, or ions from a gas or solution are attracted to the surface of a solid or liquid (adsorbent). This process is caused by intermolecular forces between the adsorbed material and the adsorbent surface.

In the context of adsorption kinetics, the aim is to understand how quickly a chemical is adsorbed and occupies the adsorption site on the surface of the adsorbent (Abd Ali *et al*., 2016; Choi, 2019; Zadeh *et al*., 2018).

2.2.1 Pseudo First Order

In adsorption kinetics, pseudo-first-order refers to a kinetic model in which the adsorption reaction rate seems to be a first-order reaction, although the actual process is more complex. This model is frequently utilized when we see that the concentration of chemicals adsorbed on the adsorbent surface declines exponentially with time. Pseudo-first-order kinetics is expressed by **Eqn. 15**.

$$\ln(Q_e - Q_t) = \ln Q_e - k_i \mathrm{t} \qquad \textbf{Eqn. 15}$$

2.2.2 Pseudo-Second Order

A pseudo-second-order kinetic model is used to model the adsorption process on the surface of the adsorbent. This model assumes that the adsorption reaction rate depends on the amount of adsorbate that has been adsorbed on the adsorbent surface which is described by **Eqn. 16**.

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 k_2} + \frac{t}{Q_e} \qquad \textbf{Eqn. 16}$$

3. Methodology

Figure 2 shows the experimental procedure in this study. Detailed information for the procedure is explained in the next session.

3.1 Materials and Chemical Reagents

In this study, several materials and chemical reagents were used, namely eggshells (obtained from Gegerkalong Market, Bandung, Indonesia); Analytical grade ammonium chloride (Purchased from Merck), Nessler's reagent (Hanna) and distilled water were used for ammonium adsorption testing.

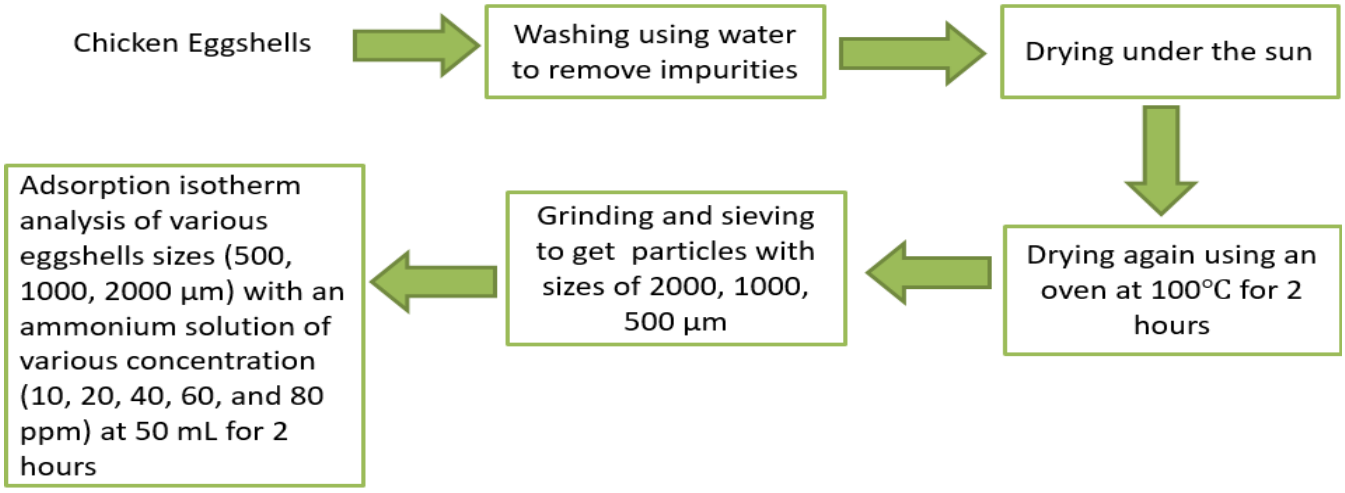

Figure 2. Schematic procedure for the experiments

3.2. Preparation of Eggshell as Adsorbent

Before use, the eggshell waste samples were first cleaned with water to remove any adhering dirt. Then dry it first under the sun. Then, the samples that had been dried in the sun were dried again in the oven at 100°C for 2 hours to ensure the samples were completely dry. To determine the distribution and specifics of the particles, the samples were sieved using mesh sizes of 2000, 1000, 500, 250, 125, 99, and 74 µm (Yayasan Bumi Publikasi Nusantara, Indonesia.)

3.3. Testing for Ammonium Elimination using Eggshell as Adsorbent

An ammonia solution was prepared with a concentration of 100 ppm as a stock solution. The procedure for making an ammonia solution with a concentration of 100 ppm is by dissolving 1 g of NH_4Cl in 1 L of distilled water. Then, the stock solution with a concentration of 100 ppm was evolved to obtain ammonium solutions with various concentrations, namely 10, 20, 40, 60, and 80 ppm. The NH_4^+ ion concentration was analyzed using the colorimetric method (Hanna HI733). Eggshells with sizes of 500, 100, and 200 µm were used in the adsorption process. The kinetics of ammonium in egg shells was also studied by observing concentrations from 0 to 2 hours, with time intervals of 10 minutes. For adsorption isotherm analysis, was carried out within 2 hours with an eggshell mass of 0.05 g of various eggshell sizes (500, 1000, and 2000 µm) with an ammonium solution of various concentrations (10, 20, 40, 60, and 80 ppm) of 50 mL at constant conditions (constant temperature and pressure).

3.4. Adsorbent Characterization

Eggshell samples were analyzed for morphology using a Digital Microscope (BXAW-AX-BC, China) to determine visualization particles. The functional group of the eggshells sample was analyzed using Fourier Transform Infrared (FTIR-4600, Jasco Corporation, Japan)

3.5. Bibliometric Analysis

To display research trends, bibliometric analysis was used in this study. Briefly, the keywords "Eggshells waste" OR "Adsorbent" OR "$CaCO_3$" of "Ammonia" were used to conduct bibliometric

analysis. The articles gathered are from 2015–2023 using Publish or Perish. Google Scholar has indexed every article that was utilized. VOSviewer was utilized to visualize the results of bibliometric analysis. Our earlier studies (Al Husaeni and Nandiyanto, 2022; Fiandini *et al*., 2023) provide further details about bibliometric analysis.

4. Results and Discussion

4.1 Bibliometric Analysis to View Publication Trends

Figure 3 shows a visualization of the network into items based on abstracts and keywords. Based on **Figure 3**, different colors can be seen, where each color represents a thematic cluster. There are 6 clusters with different colors which can be seen in **Table 3**. In **Figure 3**, the size of the nodes in each cluster is different, where "calcium carbonate", eggshell", and "waste", as well as "adsorption" have big nodes. This shows that this keyword has been widely used since 2020. Almost all other keywords are related to this keyword. Apart from that, research with the keywords "ammonia", “ammonium”, and “NH_3” have small nodes, which indicates that there has not been much research on adsorption to treat ammonia waste.

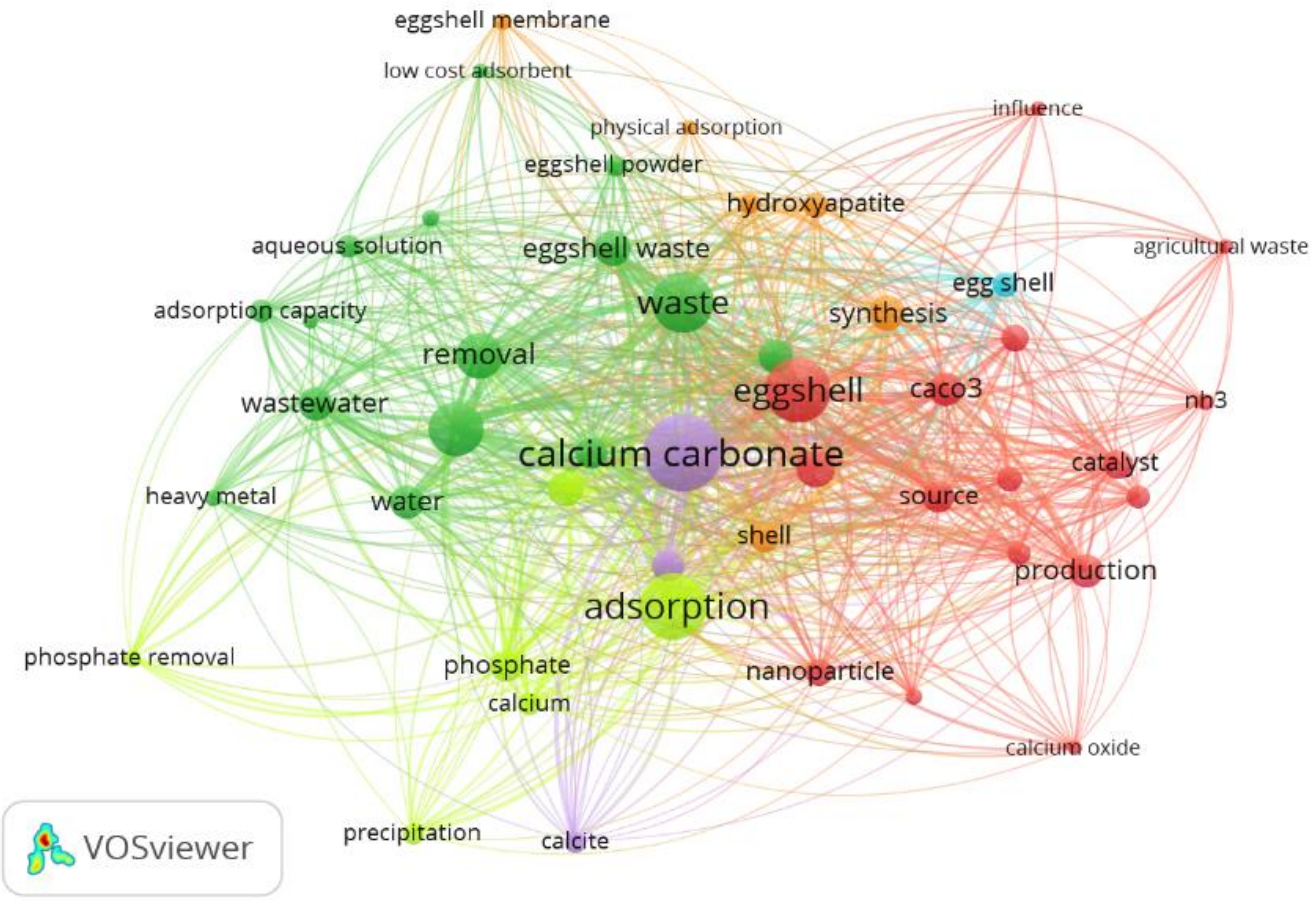

Figure 3. Network visualization based on keyword

4.2 Characterization of Adsorbent-based Eggshell

Figures 4 (a-c) represent the surface of adsorbent particles from eggshells with their distribution. There is a difference in size, what is certain is that the size of 500 μm (See **Figure 4(c)**) μm is small

compared to adsorbent particles measuring 2000 and 1000 µm (See **Figures 4(a) and (b)**, respectively). Overall, as shown in **Figures 4(a-c)**, the three sizes of adsorbent particles have irregular shapes with heterogeneous surfaces.

Table 3. Item keywords bibliometric analysis based on cluster

Cluster	Color	Item
1	Red	Agricultural waste, ammonia, $CaCO_3$, calcium oxide, CaO, carbonate, catalyst, chicken eggshell, desorption, eggshell, influence, nanoparticle, NH_3, production, source, and waste eggshell.
2	Green	Adsorbent, adsorption capacity, ammonium hydroxide, aqueous solution, eggshell powder, eggshell waste, heavy metal, low-cost adsorbent, process, removal, solution waste, wastewater, wastewater treatment, and water.
3	Orange	Eggshell membrane, hydroxyapatite, isotherm, physical adsorption, shell, and synthesis.
4	Yellow	Adsorption, ammonium, calcium, phosphate, phosphate removal, precipitation.
5	Purple	$CaCO_3$, calcite, calcium carbonate
6	Blue	Eggshell

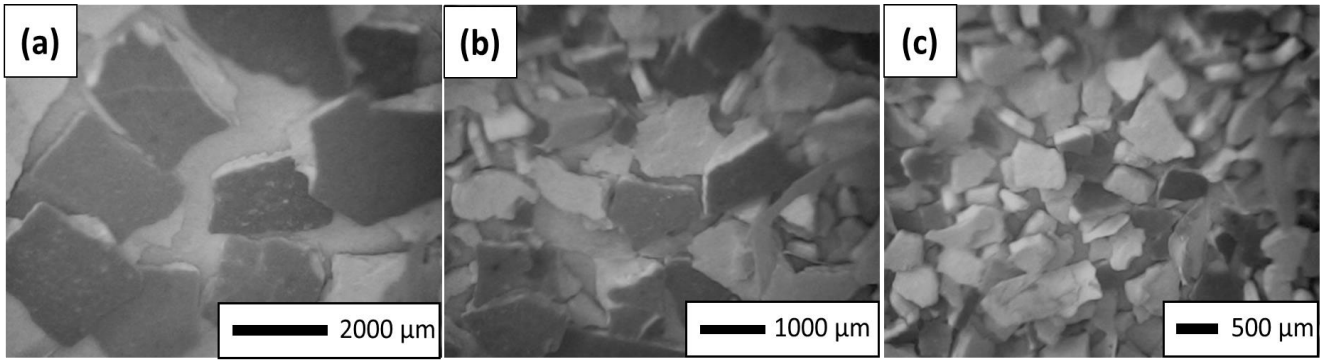

Figure 4. Digital Microscope image of adsorbent-based eggshell with their distribution (a) 2000, (b) 1000, and (c) 500 µm

FTIR was used as a secondary characterization technique to identify the presence of ammonia-adsorbed calcium carbonate ($CaCO_3$) on eggshells. The FTIR spectrum of eggshells of various sizes is shown in **Figures 5(a-c),** each of which shows six peaks. In **Figures 5 (a-c)**, there are identical peaks at all three particle sizes.

The representation of each peak, namely at 690.54-705.97 and 805.15-875.71 cm^{-1}, is a fingerprint of the vaterite CO_3 type deformation band which shows that the sample is a $CaCO_3$ variable. The absorption peak of 1575.18-1431.23 cm^{-1} indicates the presence of a CO_3^{2-} vibration mode (carbonate group) in $CaCO_3$ compounds, such as calcite, aragonite, or vaterite. These peaks are usually associated with symmetric and antisymmetric CO_3^{2-} vibrations. The absorption peak of 251.26 cm^{-1} indicates the presence of asymmetric C-H bonds and symmetric stretching, following research where the absorption peak occurs at wave numbers 2982-2876 cm^{-1}. The absorption peak at 2870.17 cm^{-1} indicates C-H bond vibration (carbon-hydrogen stretching). This is usually related to CH bonds in organic compounds. The presence of an aliphatic stretch C-H bond means that the C-H bond in the aliphatic (non-cyclic) carbon chain comes from various organic compounds, such as

aliphatic hydrocarbons, alkanes, or alkyl groups in other organic compounds. The absorption peak of 3280.43-3429.55 cm^{-1} indicates N-H bond absorption. The N-H bond absorption peak is wide with the second type of specificity. The presence of NH bond absorption indicates that ammonia is absorbed by $CaCO_3$ in the form of $(NH_4)_2CO_3$ (Hevira *et al*., 2020; Abatan *et al*., 2020; Al-Ghouti *et al*., 2018; Yusuff *et al*., 2018).

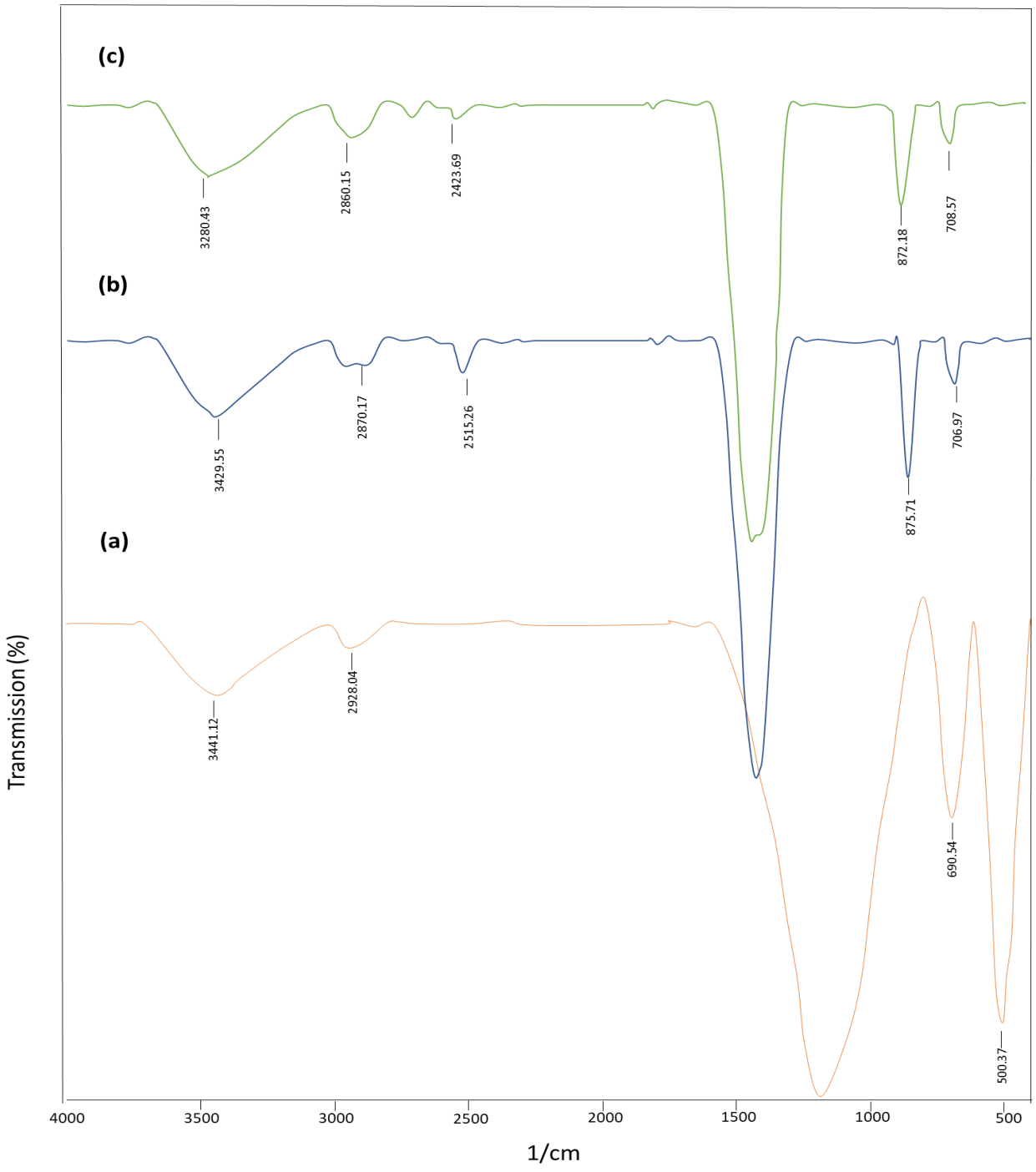

Figure 5. FTIR analysis results after adsorption with various sizes (a) 2000, (b) 1000, and (c) 500 µm

4.3. Adsorption Kinetic

To find out the rate of the ammonia removal mechanism, kinetic parameters were studied. Calculation results using **Eqn. 15** and **16** to evaluate the pseudo-first-order and pseudo-second-order

parameters shown in **Table 4**. In evaluating kinetics, the correlation coefficient (R^2) and kinetic constant parameters are used. Based on the data in **Table 4**, the pseudo-second-order has a greater correlation coefficient than the pseudo-first-order. The value of the kinetic constant shows the same thing, where the pseudo-second-order has a greater value than the pseudo-first-order. Furthermore, as shown in **Table 4**, ammonia absorption through the first pseudo order has a $Q_{(cal)}$ value that is close to $Q_{(exp)}$. These findings show that the pseudo-second-order model is most suitable. This model describes the process of the reaction rate of ammonia adsorption on eggshells as a whole depending on the difference between the amount of ammonia available and that which has been adsorbed on the surface of the eggshell. In addition, these results also confirm the existence of a mechanism involving complex formation between the adsorbate and the adsorbent surface.

Table 4. Kinetic parameters for the ammonia adsorption over eggshells

Kinetic	Parameter	Particle sizes (µm)		
		2000	1000	500
Pseudo first-order model		Q_{exp} = 0.1981		
	R^2	0.7852	0.7353	0.7944
	k_1	-0,00018	0.0053	-0.0054
	$Q_{(cal)}$	0.2745	1.0655	0.7167
Pseudo second-order model	R^2	0.8293	0.8935	0.9079
	k_2	3609.76	3898.77	3067.545
	$Q_{(cal)}$	0.2203	0.2026	0.1993

4.5. Adsorption Isotherm

Equilibrium data for ammonia adsorption using eggshell adsorbents were fitted to ten isotherm models such as Freundlich, Temkin, Dubinin-Radushkevich, Jovanovic, Halsey, Harkin Jura, Flory-Huggins, Fowler-Guggenheim, and Hill-DeBoer models. Parameter values along with statistical parameters are listed in **Table 5**. In addition, in this paper, we show only the results from the fitting curves. Detailed information for how to make fitting curve is explained in our previous studies (Ragadhita and Nandiyanto *et al.*, 2021).

The first model, Langmuir isotherm is represented in **Eqn. 1** which explains the absence of identical active sites on the monolayer surface. In this study, the Langmuir isotherm model for the three sizes had a correlation coefficient (R^2) > 0.70, indicating the suitability of the balance data with the Langmuir model. Based on the Langmuir model, the three sizes of eggshell adsorbent (i.e. 2000, 1000, and 500 µm) have a maximum adsorption capacity of 1,070; 1,139; and 1,646 mg/g, respectively. The results of the maximum capacity show that smaller particle sizes have a large maximum capacity value because they have a large surface area (Cepuritis *et al.*, 2017). From the Langmuir model, it is known that the adsorption behavior (R_L) is calculated using **Eqn. 2**. The calculation results presented in **Table 5** show that the value $0 < R_L < 1$ supports a favorable adsorption process.

The second model, the Freundlich isotherm is described by the **Eqn. 3** which represents the adsorption behavior that occurs on a heterogeneous surface. The three adsorbent sizes (i.e. 2000; 1000; and 500 µm) have a correlation coefficient (R^2) > 0.70 which confirms that adsorption occurs on heterogeneous surfaces. In **Table 5**, the adsorption intensity (n_F) values are 0.017; 0.217; and 0.304, respectively. Meanwhile, the adsorption behavior is explained by $1/n$ which explains the adsorption behavior. Based on **Table 5**, the value of $1/n > 1$ indicates cooperative adsorption

(Vigdorowitsch *et al*., 2021). The third model, Temkin isotherm is calculated using **Eqn. 4** revealing the nature of the energy required at the adsorption active site. As shown in **Table 5**, all adsorption processes for the three sizes (i.e. 2000, 1000, and 500 µm) have weak interactions between the adsorbate and the adsorbent formation chemicalsorption which is characterized by β_T > 8 kJ/mol.

The fourth model, Dubinin-Raduskhevich isotherm expressed **Eqn. 5** regarding the mechanism of the distribution of energy on a heterogeneous surface. From the data in **Table 5**, the correlation coefficient (R^2) for the three sizes is > 0.70, which indicates that there are micropores in the surface structure of the three sizes of adsorbent (i.e. 2000, 1000, and 500 µm). The free energy of adsorption to distinguish between physical and chemical properties is also studied using **Eqn. 6** and **7**. An E value > 8 kJ indicates that a physical process is occurring.

The fifth model, Jovanic isotherm explains the mechanism between adsorbate and adsorbent which results in absorption or desorbing. This model is described using the **Eqn. 8**. Based on **Table 5**, the correlation coefficient (R^2) > 0.70 which indicates the presence of a monolayer surface in the three adsorbent sizes (i.e. 2000, 1000, and 500 µm). This is in line with the Langmuir model. Apart from that, from **Table 5**, the maximum adsorption capacity is in the range of 1.151 to 5.304 mg/g.

The sixth model, the Halsey isotherm, assumes a multilayer adsorption system. This model is represented by the **Eqn. 9**. As shown in **Table 5**, the formation of a multilayer surface during the adsorption process was confirmed by a correlation coefficient (R^2) > 0.70. These results are similar to the Freundlich isotherm.

The seventh model, Harkin-Jura, describes the adsorption process that occurs in the same way as the Freundlich and Halsey isotherm. Based on the calculation results using **Eqn. 10** listed in **Table 5**, it shows the same results as those assumed by the Halsey and Freundlich model. The correlation coefficient (R^2) value is > 0.70, which indicates that adsorption forms a heterogeneous system at all sizes of adsorbent (i.e. 2000, 1000, and 500 µm). This model also explains the specific surface area (B_{HJ}). From **Table 5**, the B_{HJ} value is positive which confirms the existence of a relationship with the surface area of the adsorbent. This supports the results of the Dubinin-Raduskhevich isotherm which describes the micropore surface on the adsorbent.

The eighth model, the Flory-Huggins isotherm, explains the formation of a heterogeneous adsorbate system layer on the adsorbent surface which is described by **Eqn. 11**. In **Table 5**, all adsorbent sizes have a correlation coefficient (R^2) > 0.70, which indicates that a multilayer system has been formed. This model studies the active site of the adsorbent molecule known as the n_{FH} parameter which is calculated using **Eqn. 12**. From the data in **Table 5**, the n_{FH} value > 1 confirms that there is more than one active molecule in the heterogeneous system. Furthermore, this model also investigates the Gibbs free energy (ΔG°) which is calculated using **Eqn. 13**. The value $\Delta G^\circ < 0$ indicates that the ammonia adsorption system indicates a spontaneous system.

The ninth model, the Fowler-Guggenheim isotherm, describes the effect of lateral molecular interactions between the adsorbent and the adsorbed molecules, which is presented by **Eqn. 14**. The W parameter represents the type of interaction between the adsorbent molecules and the adsorbate. As shown in **Table 5**, for all sizes the parameter value $W < 0$ indicates the existence of attractive interactions between the particles. In addition, a negative value in the W parameter indicates that the energy conditions between the adsorbate molecules occur in endothermic conditions.

The tenth model, Hill-DeBoer isotherm explains how the movement and mutual interactions between adsorbate molecules. Investigation of interaction movements in this model was carried out using **Eqn. 14** which is symbolized by K_2. Based on **Table 5**, the K_2 parameter value > 0 indicates

that there is interactive interaction between the adsorbate particles for the three particle sizes. These results agree with the Fowler-Guggenheim isotherm.

Table 5. Isotherm models and their various evaluated parameters for the adsorption

Model	Parameter	Particle size (µm)			Note
		2000	1000	500	
Langmuir	R^2	0.934	0.877	0.782	monolayer adsorption because R^2 > 0.70
	Q_{max}	1.070	1.139	1.464	Adsorbent's maximum capacity (mg/g)
	R_L	0.214	0.596	0.760	0 < R_L < 1, the adsorption process is favorable
	K_L	0.359	0.338	0.263	Langmuir constants model
Freundlich	R^2	0.7431	0.907	0.825	multilayer adsorption because R^2 >0.70
	K_f	1.890	1.909	0.732	Adsorption isotherm Freundlich constant
	n_F	0.017	0.217	0.304	$\boldsymbol{n < 1}$, the presence of physical bonds between
	1/ n	1.098	1.091	1.106	$1/n > 1$, cooperative adsorption
Temkin	R^2	0.794	0.817	0.739	monolayer adsorption because R^2 > 0.70
	A_T (L/g)	31.914	36.376	45.236	Coefficient of binding for the Temkin equilibrium
	β_T (J/mol)	9.679	9.817	8.739	Chemical process adsorption (β_T > 8 kJ/mol)
Dubinin-Raduskhevich	R^2	0.723	0.750	0.734	multilayer adsorption process because R^2 > 0.70
	Qs (mg/g)	2.872	3.890	4.540	Capability of an adsorbent to adsorb
	β (mol^2/kJ^2)	0.789	0.536	0.893	Dubinin-Radushkevich constant
	E (kJ/mol)	0.439	0.635	0.488	Physical process adsorption (E < 8 kJ/mol)
Jovanovic	R^2	0.747	0.745	0.724	monolayer adsorption because R^2 > 0.70
	Q_{max}	1.151	1.208	5.304	Adsorbent's maximum capacity (mg/g)
	K_J	0.668	0.848	0.995	Jovanovic model constants
Halsey	R^2	0.743	0.909	0.825	Adsorption in a multilayer (R^2 > 0.7)
	N	1.345	1.100	1.212	Halsey model constants
	K_H	2.669	2.974	3.022	Halsey model constants
Harkin-Jura	R^2	0.994	0.862	0.870	Adsorption in a multilayer (R^2 > 0.7)
	A_{HJ}	1.912	0.890	0.850	Harkin-Jura model constants
	B_{HJ}	1.593	13.262	6.807	Associated with the adsorbent's surface area
Flory-Huggins	R^2	0.705	0.710	0.454	R^2 > 0.70, there is a multilayer on the adsorbent surface R^2 < 0.70, there is a monolayer on the adsorbent surface
	n_{FH}	0.164	0.002	0.006	nFH < 1, Once an active adsorbent zone meets
	K_{FH} (L/mg)	27.540	1.061	2.024	Constant Flory Huggins

	$\Delta G°$ (kJ/mol)	-0.263	-0.256	-0.351	Adsorption is spontaneous for $\Delta G° < 0$.
Fowler-Guggenheim	R^2	0.700	0.790	0.714	Adsorption in a multilayer ($R^2 > 0.7$)
	K_{FG} *(L/mg)*	22.651	18.935	12.540	Fowler-Guggenheim model constants
	W (kJ/mol)	-2.356	-2.489	-1.789	W < 0 kJ/mol, the interaction between adsorbed molecules is attractive.
Hill-DeBoer	R^2	0.987	0.854	0.934	Adsorption in a multilayer ($R^2 > 0.7$)
	K_1 (L/mg)	0.054	0.345	0.626	Constant energy for the Hill-DeBoer model
	K_2 (L/ mg)	78.642	67.263	4.675	Attraction between adsorbed species

As previously explained, from the study of the correlation coefficient (R^2) value of ammonia adsorption using eggshell adsorbents of various sizes the regarding the adsorption isotherm model were obtained as follows:

(i) 2000 µm : Hill-Deboer > Harkin Jura > Langmuir > Temkin > Jovanovic > Halsey > Freundlich, Dubinin-Raduskhevich > Fowler-Guggenheim > Flory-Huggins

(ii) 1000 µm : Halsey > Freundlich > Harkin-Jura > Hill-DeBoer > Jovanovic > Temkin > Dubinin-Raduskhevich > Flory-Huggins > Fowler-Guggenheim

(iii) 500 µm : Jovanovic > Hill-DeBoer > Harkin-Jura > Flory-Huggins > Freundlich > Langmuir > Temkin > Dubinin-Raduskhevich > Fowler-Guggenheim

Based on the results of the suitability analysis of the correlation coefficient (R^2) values, in general, the characteristics of the adsorption phenomenon for the three sizes are represented in **Figure 6.** The observation results imply that adsorption produces a single-layer system configuration with lateral interactions between the adsorbent and adsorbate. However, eggshell adsorbents are also thought to function through a multi-layered adsorption mechanism, resulting in pore filling, due to the heterogeneous distribution of the pores. In this phenomenon, a combination of phenomena was also found.

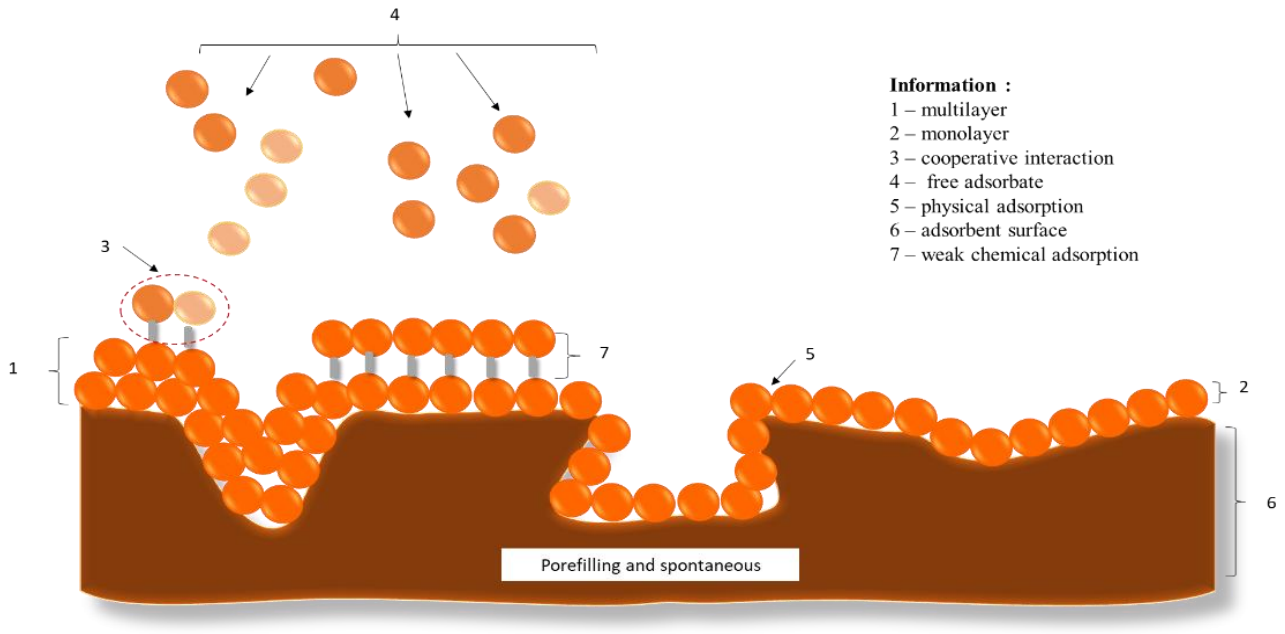

Figure 6. The phenomenon of ammonia adsorption mechanism using eggshells

Further, it was found that there was a combination of physisorption and chemisorption interactions (cooperative interactions) between the adsorbate. This result is supported by the rate of the pseudo second order adsorption process which confirms that the interaction between the adsorbate occurs in a complex manner. Even though the phenomenon confirms the chemisorption interaction, the bond is weak. However, here it is found that there is an adsorption process that occurs spontaneously because the Gibbs free energy value is negative. In this case, the adsorption capacity of the carbon adsorbent originating from eggshells is quite influenced by the particle size. As the particle size decreases, the maximum adsorption capacity of the adsorbent increases significantly. Thus, smaller particle size directly correlates with the development of a larger surface area, which results in an increased number of sites to increase adsorption capacity.

4.6. Future Research

The present study focused on the characteristics of calcium carbonate microparticles from eggshell waste. We only focused on adsorption and its phenomena. However, this study needs further analysis to confirm these phenomena. Additional data will be done in our future works, such as FTIR for samples before and after adsorption, as well as XRD, XPS, EDS, and elemental analysis. Nitrogen sorption and electron microscope are also required to ensure the porosity inside the prepared calcium carbonate.

In addition, the value of ΔG° energy in this study was obtained from the Flory-Huggins isotherm equation. Indeed, further analysis for ΔG° energy will be done, and it will need additional experiments relating to the variation of temperature.

Finally, to be applicable in industry, additional data relating to the stability of the adsorbent is needed and it will be done in our future work.

Conclusion

This study has succeeded in processing eggshell waste into an effective adsorbent for removing ammonia in polluted waste. This result is proven by the results of the adsorption rate investigation which shows harmony with the second-order pseudo model which describes the ammonia rate which depends on the availability of the amount of ammonia available and the amount of ammonia adsorbed. In addition, based on the results of the adsorption isotherm model investigation, it is informed that the adsorption process occurs by forming a multilayer layer between the adsorbent and the adsorbate which involves a complex mechanism of physisorption and chemisorption. The adsorption mechanism pattern occurs spontaneously under endothermic conditions. Not only that, this research informs that there is an effect of size shown on the difference in maximum adsorption capacity. The smaller the particle size, the greater the maximum capacity because it has a large surface area. Conversely, the smaller the particle size, the greater the maximum capacity because it has a large surface area.

Disclosure statement: This article does not contain any studies involving human or animal subjects.

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