Adsorption of Ni(II) Ion onto Calcined Eggshells: A Study of Equilibrium Adsorption Isotherm

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***Abstract:** Adsorption is one of the most effective and economical method to treat heavy metals in water. In this study, we utilize waste chicken eggshells as biosorbent to adsorb Ni(II). Furthermore we study the effect of eggshell calcination on its adsorption performance. The effect of calcination on the characteristic of eggshell was observed using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDS). It could be observed that $CaCO_3$ in eggshell was converted into CaO, and from SEM images the calcined eggshell became more porous than the uncalcined one. The effect of various parameters such as initial Ni(II) solution pH and initial Ni(II) concentration was investigated using batch adsorption experiments. The data obtained then was fitted to Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms. The best pH for Ni(II) adsorption was found to be 6. From Langmuir and Dubinin-Radushkevich isotherms, it was found that calcined eggshells gave 60 times higher maximum adsorption capacity then uncalcined one. This increase was possible due to more porous structure of calcined eggshells. The adsorption process was found to be exothermic and physisorption. This result was confirmed by the decrease of % removal with increase of temperature. Furthermore, Langmuir isotherm was found to be the best model, indicating adsorption of Ni(II) was monolayer adsorption on homogenous surface.*

***Keywords:** adsorption; adsorption isotherm; eggshells; nickel ion*

■ INTRODUCTION

Nickel is a silvery white metal that used in various industries, such as stainless steel, electroplating, battery, etc. However, the presence of nickel ion, Ni(II), in water could pose serious threat to human health and environment [1-2]. Ni (II) is known as toxicant for human, and its toxicity is depending on the exposure route. It is known as hemotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, hepatoxic, and carcinogenic [3]. According to regulation of Indonesia State Ministry of Environment No 5 (2014), the maximum acceptable limit of Ni(II) discharged wastewater is 0.5 mg/L [4]. Thus, the wastewater must be treated before being discharged to comply the limit. Various technology has been used to treat Ni(II) in water, such as precipitation, ion exchange, membrane filtration, coagulation-flocculation, and adsorption [5]. Among those technologies, adsorption using bio sorbent is known to be effective and economical method. One of potential bio sorbent is chicken eggshells.

Chicken egg is one of nutrition source, such as protein, folic acid, choline, vitamin A, B, D, E, and K [6] with high consumption in Indonesia and worldwide. In Indonesia, 1.43 million tones eggs were produced in 2016 [7], and predicted to increase in the future. This high production presents a problem because about 11%w of eggs is eggshells, which is inconsumable. Usually the eggshells are treated as waste, even though it possesses high potency for value-added products, such as nutritional supplement [8], fertilizer [6], catalyst [9], production of hydroxyapatite [10], and adsorbent [11]. Various heavy metals adsorption using eggshells has been done before, such as Cd(II) [12-13], Cr(III) [14], Cr(VI) [15], Fe(III) [16], Al(III), Fe(II), Zn(II) [17], Cu(II) [18-

19] and Pb(II) [11]. Study of comparison eggshell and calcined eggshell as adsorbent was done by Park et al. (2007) resulted on faster adsorption kinetics for Cd(II) and Cr compared to uncalcined one. Uncalcined [20-21] and calcined [22] eggshells has been used as Ni(II) adsorbent before. However, to the best of authors knowledge, the study of adsorption isotherm models has never been done before, especially for Ni(II) adsorption using uncalcined and calcined eggshells.

The aim of this study is to investigate the potential application of uncalcined and calcined eggshells for removal of Ni(II) from synthetic solution. Batch adsorption study was done to investigate the effect of initial solution's pH, initial Ni(II) concentration and temperature on Ni(II) adsorption. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms were used to analyze the equilibrium data.

EXPERIMENTAL SECTION

Preparation of Adsorbents

Chicken eggshells was collected from local market in Bandung, Indonesia. The eggshells was cleaned from the membranes, repeatedly washed to remove impurities using distilled water, and then oven dried at 110 °C for 24 h. Dried eggshells (ES) was crushed to powder to obtain particle size below 100 mesh. Calcination process was done at 850 °C for 4 h using electrical muffle furnace to obtained calcined eggshells powder (CES). Both of ES and CES were characterized using FTIR (Shimadzu FTIR, KBr pellet method) and SEM-EDS (FE-SEM, S4100. HITACHI) to observe the changes before and after calcination.

Batch Equilibrium Study

The experiment was done using batch reactor equipped with stirrer (250 rpm), in which 500 mL of Ni(II) solution ($NiSO_4.6H_2O$ from Merck, p.a) was placed. The initial pH of the Ni(II) solution was measured and adjusted using NaOH and HCl 0.1 M. Initial solution pH study was done at room temperature, and initial Ni(II) concentration of 10 mg/L, with pH variation at 2, 6, and 9. Adsorption temperature study was done at optimum pH, and initial Ni(II) concentration of 10 mg/L, while temperature was kept at room temperature (25 ± 1 °C). For confirmation of Temkin isotherm, adsorption was also done at 35 and 45 °C. The solution was heated using hotplate until the desired temperature was achieved. Adsorption isotherms study was done at optimum pH and room temperature, with variation of initial Ni(II) concentration (10, 20, 30, 50, and 60 mg/L). The amount of adsorbent used was 500 mg of ES and 10 mg of CES in this batch equilibrium study.

Five mL of sample solution was taken at initial and equilibrium to determine the concentration of Ni(II) in the solution. Before analysis, the sample was centrifuged at 6,000 rpm for 15 min. The adsorbed Ni(II) was calculated using Eq. (1), where q_e (mg/g adsorbent) was the mass of Ni(II) adsorbed per g of adsorbent, C_o and C_e (mg/L) were initial and equilibrium concentration of Ni(II) in the solution, V (L) was the volume of solution, and m (g) the mass of adsorbent used. The % removal was calculated using Eq. (2).

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (1)$$

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

Analysis of Ni(II)

The concentration of Ni(II) was analyzed using the color developing method with spectrophotometer UV/Vis measurement as described in [23] at a maximum wavelength of 470 nm. To summarize, 2 mL of sample aliquot was put in 50 mL measuring flask, then 1 mL H_2SO_4 1 M, 2 mL $Na_2C_4H_4O_6$ 20%, 8 mL $K_2S_2O_8$ 5%, 0.5 mL alkaline dimethylglyoxime (DMG) 1%, and 2.5 mL NaOH 5 N were added and made up to 50 mL using distilled water. All reagents and chemicals used were obtained from Merck with pro analysis grade. These mixtures were allowed to stand for 30 min for color development prior to spectrophotometer measurement. The Ni(II) concentration in the sample was calculated from the calibration curve prepared with standard solutions of Ni(II).

RESULTS AND DISCUSSION

Characterization of ES and CES

The morphology of ES and CES is presented in Fig. 1. It could be observed that ES sample had irregular particle shape, with small pores on its surface. After calcination, the structure changed into agglomeration of

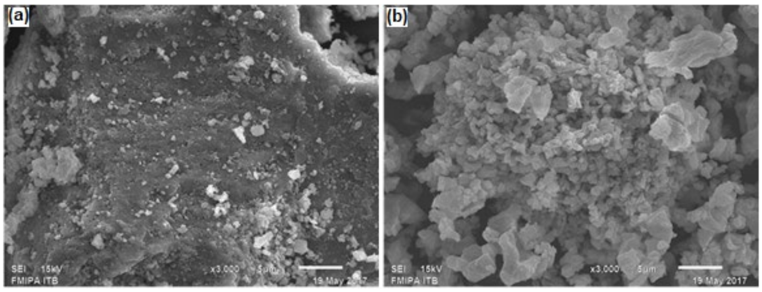

Fig 1. SEM images of ES (a) and CES (b) (magnification of 3,000×, scale bar 5 μm)

rod-like structures with bigger pores. The more developed pore structure of CES could provide higher surface area than ES [24]. Similar results were also reported in previous studies [25-27].

The effect of calcination to functional groups of eggshell was studied by FTIR spectra, presented in Fig. 2. At ES sample, it could be observed peaks at 1798 cm^{-1}, indicating carbonate C=O bond [28], 1425, 876, and 712 cm^{-1} that indicate asymmetric stretch, out of plane bend, and in-plane bend vibration of carbonate [26,29-30]. While at CES sample, it could be observe that the carbonate peaks was decreasing, and new sharp peak at 3643 cm^{-1} was formed. This peak indicates O-H stretching vibration of $Ca(OH)_2$ [28-29,31] that was formed after calcination. This result was confirmed by the SEM-EDS analysis, presented in Table 1. There was decrease of C's % mass before and after calcination process, indicating the decomposition of calcium carbonate. It is known that the eggshell was mainly composed of calcium carbonate [32], which released carbon dioxide gas during calcination, leaving CaO as the main product of the process (shown in reaction 1).

$$CaCO_3 \rightarrow CaO + CO_{2(g)} \quad (1)$$

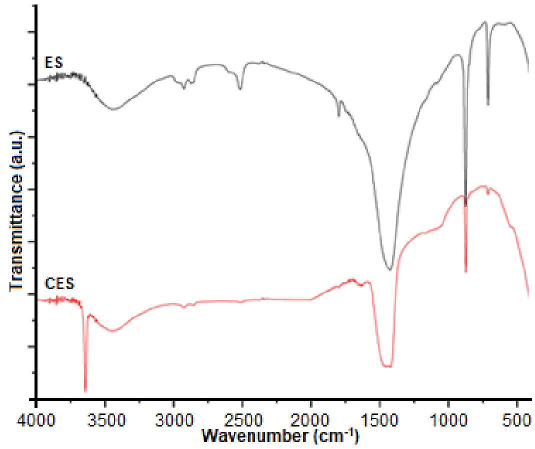

Fig 2. FTIR spectra of ES and CES

Table 1. The composition of eggshell before (ES) and after calcination (CES)

Element	% mass	
	ES	CES
C	21.32	7.23
O	53.00	53.65
Ca	25.67	36.12

Adsorption Studies

Effect of initial pH

The initial pH of solution is known as an important factor in adsorption studies. The effect of initial pH to the q_e and % removal of Ni(II) is shown in Fig. 3(a-b). It could be observed that the best initial pH condition in this experiment was at pH 6. At low pH of 2, very low q_e and % removal was obtained due to strong electrostatic repulsion between adsorbent and Ni(II) ions [33]. At low pH the adsorbent was positively charged, thus preventing adsorption of Ni(II) ions to the surface of eggshells. With the increase of pH, the q_e and % removal of Ni(II) was also increased. However at basic pH, lower q_e and % removal was observed. It was possible due to competition of OH^- and Ni(II) ions with the active sites on the adsorbents [34]. Furthermore at pH higher than 7, precipitation of Ni(II) into its hydroxides occurs [21], thus lowering the removal efficiency. The pH 6 was then used for further adsorption study.

Effect of initial Ni(II) concentration

The effect of initial concentration on the efficiency removal of Ni(II) was presented in Fig. 3(c-d). With the increase of the initial concentration of Ni(II), the % removal was decreased. This trend could happen due to with the increase of Ni(II) concentration while the adsorbent was remained constant, the adsorbent sites became saturated [33]. Furthermore, it could be observed in Fig. 3(d) that at low concentration the q_e increase linearly with the increase of C_o, at high Ni(II) concentration, the diffusion of Ni(II) was slower so that the q_e became almost constant. From the q_e vs C_o curve, it could also be observed the adsorption process following "L" isotherm, as indicated in the concave curve [35]. The "L" isotherm happens when the ratio of adsorbate concentration in the solution to the adsorbate adsorbed in the compound decreases when the solute increases, suggesting progressive saturation of the solid [35].

Equilibrium adsorption isotherm

The correlation of adsorbate concentration in the bulk phase and adsorbent at equilibrium in constant temperature is known as adsorption isotherm [35]. The study of equilibrium adsorption isotherm is usually used to provide insight to the adsorption mechanism, adsorbent's properties and characteristics, and furthermore in design of adsorption system [36]. In this study, the data obtained at room temperature was fitted to four adsorption isotherms model: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich. The fitting result is presented in Table 2 and the plot of q_e vs C_e of experimental data and calculated q_e from adsorption isotherms is presented in Fig. 4.

Langmuir isotherm

Langmuir isotherm follows assumption of monolayer adsorption with finite number of identical adsorption sites, homogenous adsorption, and no transmigration of adsorbate in the plane of adsorbent surface [36]. The equation is presented in Eq. (3), and its linearized form is shown in Eq. (4).

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (3)$$

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

From the result obtained, it could be observed that calcination of eggshell gave higher maximum adsorption capacity (q_m), with increase of 60 times. The characteristic of Langmuir isotherm could be observed from non-dimensional parameter, R_L, which calculated using Eq. (5). The value of R_L indicates irreversible ($R_L = 0$), linear ($R_L = 1$), unfavorable ($R_L > 1$), and favorable adsorption ($0 < R_L < 1$) [37].

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

It could be observed that the adsorption process of Ni(II) onto ES and CES in this study is favorable, and with R^2 value of 0.955 and 0.990 for ES and CES respectively, proving that the adsorption data was well fitted to Langmuir isotherm.

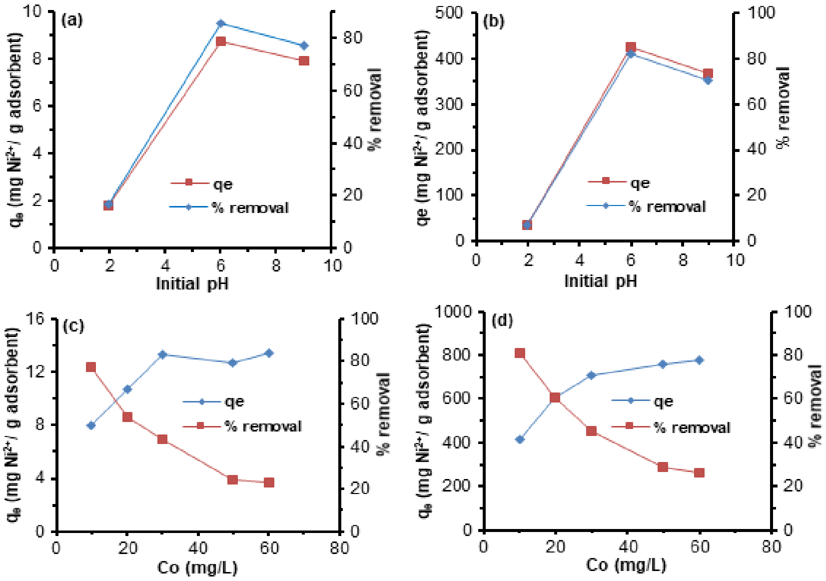

Fig 3. Effect of initial pH (a) ES, (b) CES and initial Ni(II) concentration (c) ES, (d) CES to q_e and % removal of Ni(II)

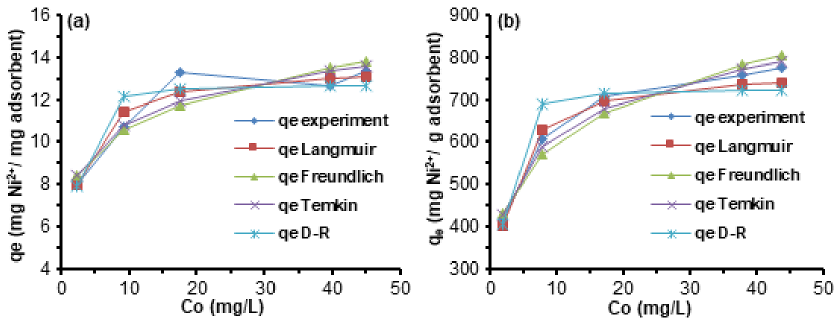

Fig 4. Plot of q_e vs C_e of experimental data and calculated q_e from various adsorption isotherm for (a) ES and (b) CES at initial solution pH 6 and room temperature

Table 2. Constants of adsorption isotherm

Isotherm	Constants	ES	CES
Langmuir	q_m (mg Ni^{2+}/g adsorbent)	13.531	769.23
	K_L (L/mg Ni^{2+})	0.6017	0.5652
	R_L	0.0276 - 0.1379	0.0289 - 0.1477
	R^2	0.9553	0.9901
Freundlich	K_f (L/mg)	7.258	378.22
	1/n	0.16807	0.20003
	R^2	0.8765	0.9578
Temkin	α (L/g adsorbent)	49.543	20.513
	β (J/mol)	1.7607	116.04
	R^2	0.8712	0.9821
Dubinin-Radushkevich	K (mol^2/J^2)	6.14×10^{-7}	5.48×10^{-7}
	q_m (mg Ni^{2+}/g adsorbent)	12.654	722.06
	E (J/mol)	902	955
	R^2	0.8762	0.9112

Freundlich isotherm

Freundlich isotherm is usually used to describe adsorption at heterogeneous surface energies, with non-ideal, reversible and multilayer adsorption process. The equation is presented in Eq. (6), and its linearized form is shown in Eq. (7).

$$q_e = K_f . C_e^{\frac{1}{n}} \quad (6)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

The K_f value indicates adsorption capacities [37], with increase of 52 times due to calcination process. The 1/n value indicates favorability of adsorption process when 0 < 1/n < 1, and cooperative adsorption when 1/n > 1 [36]. It could be observed that the adsorption of Ni(II) was favorable. The R^2 value is lower for ES (0.8762) than CES (0.9578).

Temkin isotherm

The Temkin isotherm incorporates interaction of adsorbate and adsorbent in adsorption process, also heat of adsorption (function of temperature) of molecules decrease linearly to its assumption [36]. The linearized Temkin equation is presented in Eq. (8), where α is equilibrium binding constant that represents the maximum binding energy, and β indicates the heat of adsorption [38]. Furthermore, the β could be defined as presented in Eq. (9), where R is universal gas constants, T is temperature (K), and ΔQ = (-ΔH) represents the adsorption energy [39].

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (8)$$

$$\beta = \frac{RT}{\Delta Q} \quad (9)$$

The positive β value indicates exothermic adsorption phenomenon [39-40] for both ES and CES. This result was then confirmed with a decrease of Ni(II) removal and q_e with an increase of temperature, as shown in Fig. 5.

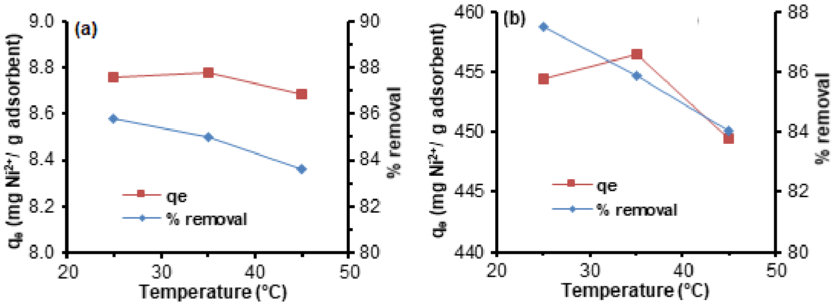

Fig 5. Effect of initial adsorption temperature (a) ES, (b) CES to q_e and % removal of Ni(II)

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich isotherm is usually used to observe the amount of adsorbed as function of adsorbate, which is assumed to be a Gaussian function of the Polanyi potential (ε) [36,41]. The linearized form and the Polanyi potential are presented in Eq. (10) and (11), respectively. This isotherm is usually used to differentiate physical and chemical adsorption of metal ions [36] by observing the mean free energy value (E), which is calculated using Eq. (12). When the E value less than 8 kJ/mol, it indicates the adsorption process is physisorption, while E value between 8 to 16 kJ/mol indicates adsorption process following ion-exchange, and the value of E in range of 20 to 40 kJ/mol indicates chemisorption [42]. The calculated E value from this study is below 8 kJ/mol, indicating the adsorption of Ni(II) onto ES and CES is following physisorption. The monolayer capacity of the adsorbent (q_m) obtained from Dubinin-Radushkevich equation was also in a good agreement with q_m value obtained by Langmuir isotherm.

$$\ln q_e = \ln q_m - K.\varepsilon^2 \quad (10)$$

$$\varepsilon = RT\ln\left(1+\frac{1}{Ce}\right)^2 \quad (11)$$

$$E = \frac{1}{\sqrt{2K}} \quad (12)$$

Based on the R^2 value presented in Table 2, it could be observed that Langmuir isotherm was best fitted for the adsorption of Ni(II) onto ES and CES compared with other isotherms. Suitability of experimental data with Langmuir isotherm indicated that the adsorbent ES and CES were homogenous, equal adsorption energy for each Ni(II) and ES/CES adsorption, as well as monolayer formation at the outer surface of the adsorbent. From the value of K_f, and also q_m, it could be observed that calcination had given significant increase to the adsorption capacity. We speculate that this increase was possible due to more porous structure that formed during calcination process, thus increasing its surface area [27]. It is known that adsorbent performance is highly dependent to its surface area.

■ CONCLUSION

In this paper, the effect of eggshell calcination to its performance as Ni(II) adsorbent was presented. The calcination had significantly increased the adsorption capacity to 60 times, observed in Langmuir and Dubinin-Radushkevich isotherm, compared with the uncalcined one. It was also observed that the adsorption process was physisorption and exothermic. Langmuir isotherm was well fitted to the experimental data, indicating monolayer adsorption onto the homogenous surface of adsorbents. This finding indicates that simple calcination process of eggshell waste could significantly increase its performance as Ni(II) adsorbent.

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