Adsorption of Heavy Metal Iron Fe(III) using Activated Powdered Duck Eggshell Adsorbent

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ABSTRACT
The purpose of this research is to study the ability of adsorption, equilibrium time, adsorption kinetics, adsorption isotherm and capacity adsorption of heavy metal such as Fe(III) using duck eggshell adsorbent. Materials that used in this research are duck eggshell adsorbent, heavy metal Fe(III), chloric acid and aquabidest. Observed variables are the equilibrium time and residual concentration of Fe(III). Adsorbent was mixed with heavy metal Fe(III) solution. The sample was being taken every 10 minutes. The concentration was analyzed with AAS (Atomic Absorption Spectrophotometer) in order to get the equilibrium concentration of heavy metal Fe(III) solution. The increasing amount of adsorbent will increase percentage adsorption and equilibrium time will be longer. Bangham model can be used to describe the kinetics of Fe (III) sorption. The Langmuir adsorption models were applied to experimental equilibrium data and the isotherm constants were calculated using linear regression analysis.

KEY WORDS: adsorbent/ adsorption/ heavy metal/ isotherm/ adsorption kinetic

1. INTRODUCTION
Nowadays there are a lot of industries generate large quantities of wastewater iron [1]. Most industrial wastewaters are discharged directly into natural water systems without proper management process [2]. These wastewaters are harmful to human’s health.

Many industries such as coating metal, car, aeronautic and steel industries generate large quantities of wastewater containing iron. It is difficult for industries to process the wastewater. In order to process the wastewater, many industries use precipitation, ion exchanger, coagulation, adsorption and ultrafiltration methods.

Therefore, the best solution for the problem is to process the wastewater. Adsorption is the best process people can choose to decrease the concentration of iron. Duck egg shell has the best adsorption properties in example pore structure, CaCO₃ and protein acid mucopolysacharide that can be developed into adsorbent [2]. The other researcher already found out that calcite from duck egg shell can be used as adsorbent to remove heavy metals.

Yeddou [3] found that dried eggshells [at 70°C] can be used to remove iron. Ruswanti [4] found that Crab’s shell can be used to make Solid Chitosan Membrane to adsorp Iron. However this method is expensive because need PVA (Poly Vinyl Alcohol) and PEG (Poly Ethylene Glycol). The purpose of this research is to study the ability of adsorption, equilibrium time, adsorption kinetics, adsorption isotherm and capacity adsorption of iron using duck eggshell adsorbent.

2. THEORY
Adsorption is a physico-chemical technique which involves mass transfer between liquid and solid phase [2]. Adsorption is an alternative method for heavy metal removal onto low cost adsorbents [1].

The specific area of adsorbents influenced the capacity adsorption of adsorbents. The larger specific area of adsorbents, the better capacity adsorption can be reached [5]. Duck eggshell used in this research has the same calcite as limestone. This calcite can remove heavy metal in solutions [6].

In this research, Bangham equation is used as adsorption kinetic. This model is used to study adsorption time and the model can be seen in equation 1 at α (<1) and kₒ is constant.

\[ \log \log \left( \frac{C_i}{C_f} \right) = \log \left( \frac{k_m}{k_o} \right) + \alpha \log t \] (1)

where \( C_i \) is the initial adsorbate concentration in solution (mg/l), \( V \) is the volume solution (ml), \( m \) is the adsorbent mass per liter solution (g/L), \( q_e \) is the amount of adsorbent that has been adsorbed at t min (mg/g) and \( k_o \) is the constants of Bangham equation [7].

The Langmuir isotherm has a theoretical basis and is given by the following, where \( q_m \) and \( K \) are empirical constants.

\[ q_e = \frac{b q_m C_i}{1 + b C_i} \] (2)

This equation is linearised into equation 3.
\[ \frac{C_e}{q_e} = \frac{1}{q_m} + \left( \frac{1}{b q_m} \right) C_e \]  

where \( C_e \) is adsorbate concentration at equilibrium in liquid phase (mg/L), \( q_e \) is adsorbate concentration at adsorbent (mg), \( 1/q_m \) is slope, \( q_m \) is optimum adsorption capacity (mg/g), \( 1/b q_m \) is intercept and \( b q_m \) is equilibrium constants \[3\].

The equation was derived assuming that there are only a fixed number of active sites available for adsorption, only a monolayer is formed, and the adsorption is reversible and reaches an equilibrium condition. By plotting \( C_e/q_e \) versus \( C_e \), the slope is \( 1/q_m \) and the intercept is \( 1/b q_m \) \[8\] \[3\].

3. MATERIALS AND METHOD

3.1 Materials

Materials that used in this research are duck eggshell adsorbent that has been activated at 600°C, heavy metal (iron) solution, double-distilled water (dd-H₂O) and hydrochloric acid (HCl).

3.2 The Removal of Iron Using Duck Eggshell

Heavy metal solution was added into three beaker glasses 1000 ml and the initial concentration of solution was 12.5 ppm. Then in each beaker glass, a certain amount of adsorbent was added. The magnetic stirrer was adjusted at 300 rpm. Every 10 minutes the sample was filtered through filter paper and then the iron concentration was determined.

4. RESULT AND DISCUSSION

According to the research has been done by Jasinda [9], is known that surface area of duck eggshell adsorbent is 2700.978 m²/g. This surface area was examined with metilen blue such as Putra [1] procedure.

4.1 Effect of eggshell dosage

The effect of the eggshell dosage on the removal of Fe(III) is shown in Fig. 1. The adsorbent dosage was varied from 0.5 gr/L to 1.5 gr/L.

According to the results from Ghazy [10], Nurhasni [11] and Siti [12], increasing the amount of adsorbent will decrease heavy metal concentration in solution. This means that the percentage adsorption will be enhanced with the higher dosage of the adsorbent. In the present research, the phenomena are same as the results of Ghazy [10], Nurhasni [11] and Siti [12] research.

The equilibrium time will take longer as the amount of adsorbent is increased. This phenomena occurs since the tendency of the molecules to escape from the adsorbent surface to the solution phase was increased. The tendency will occur because the intermolecular attraction force between molecules of an adsorbent and the heavy metals was weaker. The intermolecular attraction force are Van der Walls, diffusion and dipole – dipole.

4.2 Determination of Adsorption Kinetics

Fig. 2 is a graph that shows the adsorption kinetics in this research.

According to the results, the numbers of active sites available for adsorption, only a monolayer is formed, and the adsorption is reversible and reaches an equilibrium condition. By plotting \( C_e/q_e \) versus \( C_e \), the slope is \( 1/q_m \) and the intercept is \( 1/b q_m \) \[8\] \[3\].
value of $k_m$ is 1.3818. Bangham equation is a kinetics equation that is used in adsorption process.

4.3 Determination of Adsorption Isotherm and Capacity of Adsorption

Fig. 3 shows the pattern of adsorption isotherm. Fig. 4 was plotted for the Langmuir isotherm model. The Langmuir isotherm was found to be the best-fitting isotherm with $R^2$ is 0.9084. The Langmuir constants $b_m$ and $q_m$ can be calculated from the plot between $C_e/q_e$ vs $C_e$. The value of $b_m$ is 4.1911 and $q_m$ is 9.0334. The Langmuir isotherm models were applied to the experimental equilibrium data for iron sorption at different temperature [1].

Capacity of adsorption shows the number of active binding sites on the adsorbent surface. The value of experimental equilibrium adsorption capacity ($q_m$) is 9.0334 mg/g. This is the value of Langmuir constants which unit is mg/g. The experimental equilibrium adsorption capacity shows the adsorption capacity at room temperature and the initial concentration is 12.5 ppm using duck eggshell adsorbent.

![Fig. 3 Pattern of Adsorption Isotherm for Iron Ion](image)

![Fig. 4 Langmuir Isotherm Model for Adsorption of Iron Ion onto Duck Eggshell Adsorbent](image)

4. CONCLUSION

Adsorption Percentage shows the ability of duck eggshell adsorbent adsorps heavy metals. At 1.5 gram of adsorbents, we can get the maximum adsorption percentage is 65.0435%.

In this research, the greater amount of adsorbent used, the equilibrium time will be slower to reach. And the greater amount of adsorbent used, the percentage of adsorption increased.

Sorption of iron ion onto duck eggshell adsorbent follows the Bangham kinetics. The Langmuir isotherm model is appropriate to describe the sorption of the Fe (III) ion on the duck eggshell adsorbent. Capacity of adsorption of iron is 9.0334 mg/g.

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