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Langmuir and Freundlich Isotherm Approximation on Adsorption Mechanism of Chrome Waste by Using Tofu Dregs

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ABSTRACT

The requirement to discover low-cost and high-efficiency adsorbents material for the heavy metal removal of industrial effluents has been growing attention for many environmental researchers. Natural materials are being studied intensively as adsorbent materials because of their abundant source, low-cost processing, and relatively high adsorption efficiency. This study investigates the tofu dregs as adsorbents material to remove chrome metal, the main element in tannery liquid waste. Analysis of experimental data from adsorption processes is crucial to understand and predict removal mechanisms, efficiency, or required adsorbent mass under given initial conditions. Langmuir and Freundlich's adsorption isotherms were applied to the experimental data to determine their intrinsic parameters. The intrinsic parameters of Langmuir and Freundlich adsorption isotherms can subsequently be used to analyze the adsorption mechanism. This was achieved by combining the isotherms equation with mass conservation of solute before and after adsorption

Keywords: Langmuir isotherm, Freundlich isotherm, intrinsic parameters chrome, mass conservation, tofu dregs

Introduction

Chromium (Cr) specifically, trivalent chromium Cr(III), is an essential element many people use as a supplement. Chromium can form a compound in the body that enhances the effects of insulin for diabetes therapy by lowering glucose levels. However, it also has risks if maximum excess content in the human body affects cholesterol, heart disease, psychological disorders, and Parkinson's disease. The recommended dietary allowance (RDA) for chromium is still unclear. But depending on the age minimum, expert estimates the amount of chromium that people should get ranging from 20-35 μg/day, mostly from food. The additional quantity of Cr in the environment may cause uncontrollable Cr in the human body (WHO, 1996).

Chromium salts and metal chromium are widely used in industries, such as the leather tanning industry, pigments and paints, fungicides, ceramic and glass industry, and chrome plating for corrosion control (WHO, 1990). The leather tanning industry is one of the industries with a large amount of waste. The main content is chromium (60-70%). It comes from the tanning process using chromium sulfate (Ma'mun et al., 2016). Chromium sulfate solutions were used as salts on tanning hide into leather, unabsorbed chromium sulfate by the skin is excreted in liquid waste. Generally, solution-phase chromium in trivalent chromium Cr(III) ionic is its stable ionic state.

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Still, it can be oxidized into hexavalent Cr(VI) ions depending on the redox potential energy of oxidizing compounds and the kinetics of the redox reactions. Hexavalent Cr(VI) ion is toxic and carcinogenic. Cr(VI) readily penetrates cell membranes and is subsequently reduced to Cr(III) and binds to macromolecules. Exposure to water containing Cr(VI) can cause tumors, mutations, and chromosomal breaks. Moreover, the Cr(VI) ions in salt form have high solubility in water than those of Cr(III), which causes effective migration of Cr(VI) in aqueous media.

The existing regulation on maximum acceptable concentration (MAC) of chromium in water is 50 µg/L (WHO, 1996). Several methods have been addressed to reduce Cr concentration in wastewater before releasing it into the environment. For example, coagulation is followed by filtration, ion exchange, adsorption, and membrane filtration. Coagulation followed by the filtration method is relatively expensive and produces a high volume of sludge. Similarly, membrane filtration requires high operational costs. While, the removal efficiency of the ion exchange method is affected by the presence of another ion in water (Zhitkovich, 2011). Adsorption onto adsorbent material method over several advantages compared to other methods such us; effective to remove both Cr(III) and Cr(VI) and other heavy metals and organic micro-pollutants.

Furthermore, due to the ability of macromolecular (protein) to bind Cr(III), high cell membrane penetration, and repeat reduction of Cr(VI) to Cr(III), the organic molecular potential to be used as adsorbent media, which is known as bio-adsorbents. The protein surface is covered by a series of functional sites capable of binding metal ions or other molecules. Functional sites include carboxyl, amino acids, carbonyl, hydroxyl, alcohol, amine, ester, sulfides, etc. Large amounts of types and sources of bio-adsorbent materials are continuously produced in some countries, which offers a reliable source to be used as a low-cost adsorbent material (Kampalanonwat et al., 2014).

Dry tofu has been reported to show a high adsorption capacity of orthophosphate (PO_4^{3-}) compared to its adsorption onto calcium carbonate. Another study also showed a high adsorption capacity of Fe and Pb, 95.53% and Pb, 98.03%, respectively (Nohong, 2010). The high adsorption capacity of tofu may be due to its high macromolecular contain. In this study, we use tofu dregs as a replacement for tofu as adsorbent. Tofu dregs are the residue from the soybean filtering during tofu processing. Tofu dregs are assumed to have the same macromolecular contain as tofu, making it a good alternative as low-cost adsorbent material.

A proper understanding and interpretation of the adsorption mechanism are critical for the overall improvement of the adsorption process and an effective design of the adsorption system; adsorbent properties, required mass of adsorbent, initial and expected final solution concentration. Several approximations have been applied to evaluate the adsorption mechanism of adsorbent material. In this study, we use Langmuir and Freundlich isotherms approximation to understand the adsorption mechanism of tofu dregs. These analyses are the most applied approximation for the initial adsorption study and defining the best adsorption models because of their simplicity and ability to quantify the distribution of functional sites of adsorbent. Langmuir-type adsorption is a monolayer (surface) adsorption, which implies that a large surface area will result in a higher adsorption capacity. Freundlich-type adsorption is considered a multilayer adsorption process (Ayawei et al., 2017).

The experiment result gives adsorption data at an equilibrium state, which is essential to understand an adsorption process. Generally, experimental data were plotted to the adsorption models, and the best-fitted model was then used to determine adsorption models. As the appropriate adsorption model was found, the adsorption parameters can describe the adsorption characteristics. The objective of this study was to demonstrate how basic adsorption isotherms combined with simple mass conservation of solute can be used to analyze the adsorption mechanism.

Material and Methods

Preparation of tofu dregs and Adsorption Process

Tofu dregs powder for the adsorption of chromium was prepared by drying it through the sunlight irradiation for three days, followed by heating at 60 °C for 14 hours in an oven. The dry tofu dregs then ground with a blender, large particles were removed by using a 60-mesh sieve. The leather tanning waste was taken from UPT Industri Kulit dan Produk Kulit Magetan, East Java. Before being used as a waste solution to be adsorbed by using tofu dregs, the leather tanning waste was filtered to obtain a sediment-free solution. NaOH and HCl solution is used to adjust the waste solution pH, pH = 7.

The adsorption tests were carried out by varying the mass of the tofu dregs powder; 1.2, 2.4, 3.6, 4.8, and 6 g, and separately added to 600 ml of waste solution. The mixed solution was then stirred at a constant temperature and stirring speed of 50 °C and 200 rpm, respectively, with a different contact time of 40, 70, 100, 130, and 160 minutes. The tofu dregs powder in each sample was filtered out using a 60-mesh sieve before measuring absorbance to evaluate the equilibrium concentration of chromium in solution Atomic Absorption Spectrophotometer (AAS) where applied.

Model development of Langmuir isotherm

The Langmuir isotherm adsorption, which was primarily constructed to describe gas-solid phase adsorption, is also widely used to evaluate the adsorption capacity of solved solid particles onto a solid surface, liquid-solid phase adsorption. The adsorption capacity of Langmuir isotherm approximation is proportional to the surface area of solid coverage by functional sites, where functional sites can bind the solute. The Langmuir isotherm equation is expressed by the following equation (Dabrowski, 2001):

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

where Ce is the solute concentration in the solution at equilibrium (mg/L), q_e is the solute mass adsorbed per unit adsorbent mass at the equilibrium state (mg/g), q_m relates to the maximum adsorption capacity (mg/g), and K_L is the Langmuir isotherm constant (L/mg). The above equation can be rewritten in the linear equation as follow:

$$\frac{1}{q_e} = \left(\frac{1}{K_L \cdot q_m}\right) \cdot \frac{1}{C_e} + \frac{1}{q_m} \qquad (2)$$

The C_e is directly obtained during adsorption measurement, while q_e can be calculated for a series of different initial conditions, then $1/q_e$ can be plotted linearly as a function of $1/C_e$. The Langmuir isotherm parameter, K_L, and q_m, can be obtained using the slope and the intercept, respectively. This tow parameter is the intrinsic parameter of adsorbent material, which depends on adsorbent and solute characteristics, type, and distribution of the functional sites and solute. If the resulting plot is perceptible linear, the adsorption process can be assumed to follow the Langmuir adsorption isotherm.

It should be pointed out that, in the Langmuir isotherms adsorption linear equation, Eq. (2), the amount of adsorbed solute per unit adsorbent mass (q_e) is expressed as a function of the solute concentration at equilibrium (C_e). It means that the Langmuir isotherms adsorption equation would only be utilized when the solute concentration at equilibrium is known. However, in practical adsorption implementation, it might be more desirable to predict the adsorption capacity for the given initial set of conditions, such as initial solute concentration (C_0), solution volume (V), and adsorbent mass (M). Few studies have been conducted to directly predict adsorption capacity as functions of the initial set of adsorption conditions that could be conveniently applied to actual adsorption processes. Chung *et al.* developed a method to predict removal efficiencies of oyster shell powder. However, in this study, we use the same approach to analyze the adsorption mechanism of tofu dregs powder.

The mass conservation of solute at the given solution volume should be satisfied the following equation (Chung et al., 2015):

$$C_0 = C_e + C_e^s \qquad (3)$$

where the symbol C_0 is the initial concentration of solute, and C_e^s means the concentration of solute adsorbed onto the adsorbent at the equilibrium state. The q_e can also be expressed in terms of solution volume and adsorbent mass, as follows:

$$q_e = \frac{VC_e^s}{M} = \frac{V(C_0 - C_e)}{M} \qquad (4)$$

The linear Langmuir isotherm equation, Eq. (2) combined with Eq. (4) gives the second-order function of solute concentration at equilibrium (C_e) as follows:

$$K_L C_e^2 + (1 + K_L q_m M/V - K_L C_0)C_e - C_0 = 0 \qquad (5)$$

The resulting equation shows that the concentration at equilibrium (C_e) is a quadratic function of the independent initial set of conditions (C_0, V, and M) and intrinsic parameters (K_L and q_m). If all of these variables remain constants, and thus C_e can be explicitly and solved by using the quadratic formula:

$$(C_e)_{1,2} = \frac{-(1 + K_L q_m M/V - K_L C_0) \pm \sqrt{(1 + K_L q_m M/V - K_L C_0)^2 + 4K_L C_0}}{2K_L} \qquad (6)$$

Only C_e with positive value has meant, so the solution is as follows:

$$C_e = \frac{-(1 + K_L q_m M/V - K_L C_0) + \sqrt{(1 + K_L q_m M/V - K_L C_0)^2 + 4K_L C_0}}{2K_L} \qquad (7)$$

From this equation, we can see that only positive K_L gives physical meaning, satisfying the Gibbs free energy ($\Delta G°$), as shown in Eq. (8), where negative K_L resulted from imaginer Gibbs free energy.

$$\Delta G° = -2.303 \cdot RT \log K_L \qquad (8)$$

Model development Freundlich isotherm

The Freundlich isotherm adsorption was constructed to describe both gas-solid phase adsorption and liquid-solid phase adsorption. If the adsorption follows the Freundlich isotherm, we can assume that the adsorbent surface is heterogeneous. This isotherm adsorption approximation gives an expression that defines the surface heterogeneity and the exponential distribution of functional sites. Freundlich isotherm adsorption is also considered to be a multilayer adsorption process. The Freundlich isotherm equation can be expressed by the following equation (Edzwald, 2011):

$$q_e = K_F C_e^{1/n} \qquad (9)$$

where K_F is the Freundlich isotherm constant ($L^{1/n} mg^{(1-1/n)}/g$) and $1/n$ is the Freundlich exponent. K_F and n are constants that depend on adsorbent and solute characteristics and the heterogeneity of the adsorbent sites. The linear form of the Freundlich isotherm can be formulated as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (10)$$

Similar to the Langmuir adsorption isotherm, the above linear form of the equation can evaluate whether the adsorption process satisfies the Freundlich isotherm and identifies the constants. According to the equation, Eq. (10), if the resulting plot is perceptible linear, the adsorption process can be assumed to follow the Freundlich adsorption isotherm.

Results and Discussion

The experimental data of chromium adsorption onto tofu dregs powder for 70 minutes contact time were fitted to the linear forms of isotherms Eq. (2) and (10) to determine intrinsic parameters of Langmuir and Freundlich isotherm, which are graphically represented in Fig. 1. From the intercept and slope of the linearized plot of q_e against C_e in Fig. 1(a), the K_L and q_m values for variation of contact time were obtained as listed in Table 1. While the linearized plot of log q_e against log C_e in Fig. 1(b), the K_F and $1/n$ values for variation of contact time were obtained as listed in Table 2. The linearized plot in Fig 1 indicates that the Langmuir equation, rather than the Freundlich equation, provided an excellent mathematical approximation to describe the adsorption equilibrium, where the Langmuir plot in Fig. 1(a) fitted the experimental data with $R^2 = 0.993$, which suggested the monolayer adsorption, while Freundlich plot in Fig. 1(b) has a coefficient of determination $R^2 = 0.9494$.

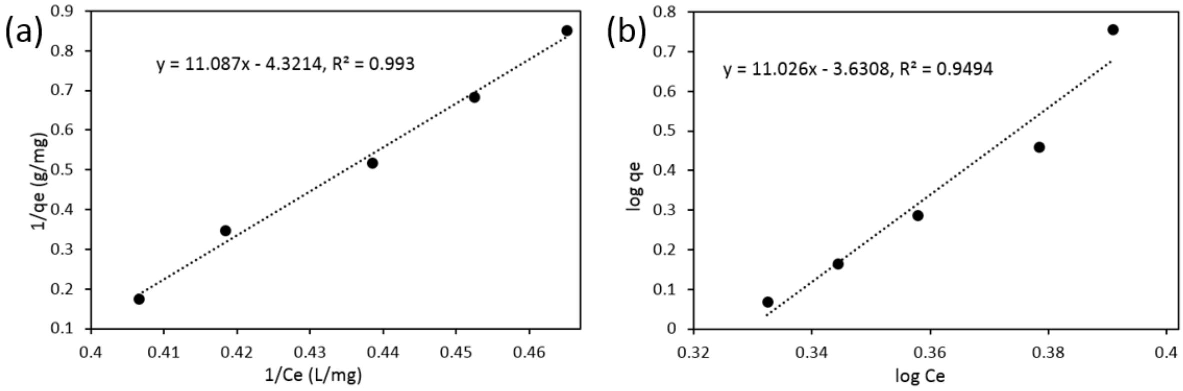

Figure 1. Experimental data of chromium adsorption onto tofu dregs powder fitted to linearized forms of (a) Langmuir and (b) Freundlich adsorption isotherm with 70 minutes contact time.

From the intrinsic parameter can be concluded that the Freundlich equation is more suitable to describe the adsorption mechanism, where the linearized plot for all contact times gives the positive value of K_F and $1/n$. In contrast, Langmuir equation, all linearized plots give the negative value of K_L and q_m, as listed in Table 2 and Table 1, respectively, and therefore, adsorption is suitable for the heterogeneous surface.

Table 1. Langmuir adsorption isotherm parameters determined from linear plotted experimental data.

Contact time (minute)	K_L (L/mg)	q_m (mg/g)	R^2
40	-0.1613	-0.56689	0.9721
70	-0.38977	-0.23141	0.993
100	-0.48835	-0.39061	0.9951
130	-0.61755	-0.95484	0.9831
160	-0.67754	-4.49843	0.9736

Table 2. Freundlich adsorption isotherm parameters determined from linear plotted experimental data.

Contact time (minute)	K_F $(L^{1/n}mg^{(1-1/n)}/g)$	$1/n$	R^2
40	0.0022	4.3977	0.912
70	0.00023	11.026	0.9494
100	0.0438	7.3051	0.9544
130	1.533	3.8124	0.9396
160	8.266	1.7581	0.9307

Significant total adsorption occurs at low adsorbent mass, $M \leq 1.2$ g, but the increase in the amount adsorbed mass, $M > 1.2$ g, with constant initial Cr concentration adsorption becomes saturated and less significant, which are graphically represented in Fig. 2. This result is probably due to spontaneous adsorption at all available functional sites. At small amounts of adsorbent, relatively all functional sites at the adsorbent surface can bind Cr ions. In contrast, not all functional sites can bind Cr ion by increasing adsorbent mass at constant initial Cr concentration, therefore adsorption at saturation condition.

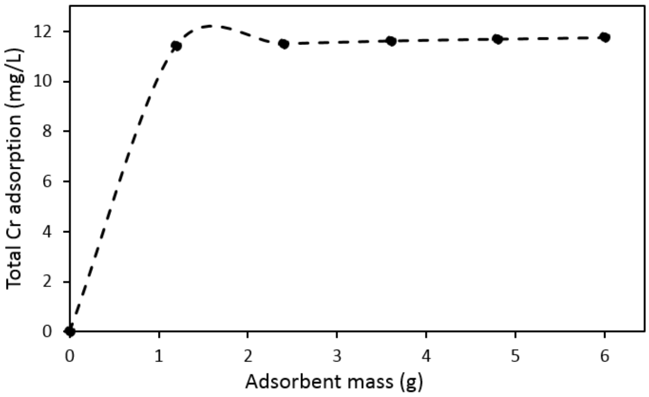

Figure 2. Total chromium adsorption as a function of tofu dregs powder mass with 70 minutes contact time.

Although the Langmuir isotherm plot fitted the experimental data with $R^2 = 0.993$, the intrinsic parameter KL and qm do not give physical meaning or negative values, which does not satisfy the Gibbs free energy ($\Delta G°$), indication that effective adsorption takes place at low adsorbent mass. Negative K_L means that at high addition of adsorbent mass, adsorption does not follow Langmuir assumptions. The adsorption capacity reaches a specific limit by increasing the adsorbent mass at a certain point. Therefore another isotherm approximation should be applied.

Conclusion

We can conclude that the adsorption mechanism can be determined using Langmuir and Freundlich's adsorption isotherm equation derivation and combined with the mass conservation of solute before and after adsorption. Linear plots of Langmuir and Freundlich isotherms show well-fitted experimental data with a coefficient of determination is $R^2 > 0.9$, suggesting that both approximations are suitable for describing the adsorption mechanism. However, the intrinsic parameters of Langmuir isotherm have a negative value. It is maybe due to an ineffective functional site at the adsorbent surface to bind Cr ion at the high amount of adsorbent mass.

Consequently, adsorption reaches the saturation point. For the future study of tofu dregs adsorption, variation of initial concentration of Cr and low addition of adsorbent mass, M < 1.2 g, required to understand adsorption mechanism and at high addition of adsorbent mass another isotherm approximation should be applied.

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