Adsorption laboratory experiment for undergraduate chemical engineering: Introducing kinetic, equilibrium and thermodynamic concepts

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Abstract. Adsorption laboratory experiment for undergraduate chemical engineering program is discussed. The experiment demonstrated adsorption of copper ions commonly found in wastewater using bio-sorbent, i.e. agricultural wastes. The adsorption was performed in a batch mode under various parameters: adsorption time (up to 120 min), initial pH (2 to 6), adsorbent dose (2.0 to 12.0 g L\(^{-1}\)), adsorbent size (50 to 170 mesh), initial Cu\(^{2+}\) concentration (25 to 100 ppm) and temperatures (room temp to 40\(^{\circ}\)C). The equilibrium and kinetic data of the experiments were calculated using the two commonly used isotherms: Langmuir and Lagergren pseudo-first-order kinetics. The maximum adsorption capacity for Cu\(^{2+}\) was found as 94.34 mg g\(^{-1}\). Thermodynamically, the adsorption process was spontaneous and endothermic. The calculated activation energy for the adsorption was observed as high as 127.94 kJ mol\(^{-1}\). Pedagogically, the experiment was assumed to be important in increasing student understanding of kinetic, equilibrium and thermodynamic concepts.

1. Introduction
Adsorption is one of the methods frequently used in pollution prevention processes, especially in wastewater treatment, as it is considered to have several advantages compared to other methods such as chemical precipitation, coagulation-flocculation, ion exchange etc [1]. Wastewater may contain hazardous metal ions such as Cu\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\) etc., and adsorption using agricultural wastes has been an extensive area of research to remove the metals [1-7]. In such a case, the adsorption method is seen as environmentally friendly.

Students may have a basic understanding of adsorption [8]. However, they may have not realized that adsorption involves basic concepts such as equilibrium, kinetic and thermodynamic. In this paper, a laboratory experiment on adsorption of Cu\(^{2+}\) using powder of dried teak (Tectona grandis sp) leaves is discussed. The experiment was carried out with the intention to enhance student understanding on the concept of equilibrium, kinetic and thermodynamic. Two undergraduate students conducted the experiment, analyzed the data obtained, plotted the graphs etc under the supervision of the authors. The experimental results were discussed in terms of two adsorption isotherms, i.e. Langmuir and Freundlich models, which are regarded as convenient in describing experimental results over a wide range of concentrations [9].

2. Materials and Methods
2.1. Dried powder leaf preparation
Fallen leaves of Tectona grandis sp were collected locally, i.e. from UNTAG University yard and gardens. These samples were washed extensively with tap water to remove dust and other particulates, followed by rinsing with distilled water. The cleaned leaves were then oven-dried (60\(^{\circ}\)C, 24 h) until constant weight was obtained. The resulting samples were pulverized using a household blender and sieved to obtain powder of the following sieve-cuts: 50-80, 80-100, and 100-170 mesh. The sieved
powder, named teak leaves powder (= TLP), was stored in air-tight plastic containers according to their size for subsequent used as adsorbents.

2.2. Preparation of stock solutions
Stock solution of 1,000 mg L\(^{-1}\) concentration of Cu\(^{2+}\) was prepared by dissolving 4.785 g of CuCl\(_2\)·6H\(_2\)O in doubly distilled water to obtain a volume of 1,000 ml. The experimental solutions of varying concentrations were obtained by successive dilution of the stock solution. The pH of the experimental solutions was adjusted to the desired values with 0.1 M HCl. All chemicals used were analytical grade and used without further purification.

2.3. Adsorption experiment
Batch adsorption experiments were carried out to investigate the effect of initial pH of solution, adsorbent dose, adsorbent particle size, initial metal ion concentration, contact time and temperature on the adsorption of Cu\(^{2+}\) on TLP.

In all experiments, fixed volume (100 mL) of Cu(II) were placed in conical flasks and thoroughly mixed with TLP of varying sizes and dose and stirred with varying speed (100 to 250 rpm). The experiments were done at different temperatures (ambient, 30, 40\(^{\circ}\)C) for up to 120 min. Different conditions of initial pH of the solution (2.0; 4.0; 6.0) were evaluated. At the end of the adsorption run the solutions were filtered through ash-less filter paper.

The concentrations of Cu\(^{2+}\) remaining in the filtrates were analyzed using flame atomic absorption spectrophotometer (AAS-Varian, AA240). The percentage adsorption of Cu\(^{2+}\) adsorbed from the solution by TLP was calculated using the following (Eq. 1):

\[
\% \text{ adsorption} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium Cu\(^{2+}\) concentration (mg L\(^{-1}\)), respectively.

The amount of Cu\(^{2+}\) adsorbed at time t, i.e. \(q_t\) (mg g\(^{-1}\)) was calculated as follows (Eq.2):

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

where
\(C_t\) = concentration of Cu\(^{2+}\) at time t, (mg L\(^{-1}\)),
\(V\) = volume of solution, L,
\(m\) = mass of TLP, g.

The adsorption at equilibrium, \(q_e\) (mg g\(^{-1}\)) was measured using Eq (3) as follows:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

Calibration curves of standard solutions of Cu\(^{2+}\) were used to calculate the Cu\(^{2+}\) concentrations. The experimental data were fitted to two adsorption models namely, Langmuir and Freundlich.

3. Results and discussion
3.1. Effect of initial pH, adsorbent size, agitation and adsorbent dose
Variation in pH leads to variation in the metal ion speciation and the dissociation of active functional sites on the adsorbent [3,4]. Further, different metal ions would show different optimum pH for adsorption, as would different biomass [5]. The effectiveness of Cu\(^{2+}\) adsorption by TLP as a function of pH is plotted (Figure 1-a).
As can be seen (Figure 1-a), for all adsorbent sizes (50-80 mesh; 80-100 mesh; 100-170 mesh), a steady increase in adsorption with increasing pH is observed up to pH 6.0. Beyond 6.0, the adsorption capacity decreases, indicating that pH = 6.0 is the optimum. Further, as adsorption is a surface phenomenon, the smaller adsorbent sizes (= higher mesh) offer higher adsorption capacity due to the availability of relatively larger surface area. Depending on the adsorbent size, the increase in adsorption rises from 15% (pH 2.0) up to 77% (pH 6.0).

The effect of agitation speed on the adsorption of Cu^{2+} was carried out for pH = 6.0, with TLP size cuts of 100 to 170 mesh, for a fixed initial concentration of 100 mg L^{-1} of Cu^{2+} at room temperature (Figure 1-b). As shown, the adsorption capacity of TLP increased from 21% up to 85%. The effect of increased agitation speed can be attributed to the decrease in the boundary layer thickness surrounding TLP particles [4, 6], hence increased more adsorption.

For a fixed particle size, the amount of adsorbent correlates linearly with available surface area for adsorption. As can be seen the percentage of adsorption of Cu^{2+} increases dramatically with increasing TLP dose up to 10 g L^{-1} (Figure 1-c). This can be due to the availability of more adsorption sites with the increased dosage. However, beyond 10 g L^{-1}, the percentage removal remained relatively constant. This phenomenon can be attributed to the attainment of equilibrium in the system [3].
### 3.2. Adsorption models

Isotherm models would show the distribution of adsorbate (= Cu$^{2+}$) between the solution and the TLP particles. The isotherm models most widely used to describe the adsorption processes, i.e. the Langmuir and Freundlich isotherms relate the rate adsorption density, $q_e$, (= Cu$^{2+}$ uptake per unit weight of TLP) to equilibrium Cu$^{2+}$ concentration in the bulk liquid phase, $C_e$.

The Langmuir adsorption isotherm model suggests a uniform surface and that the adsorbate uptake occurs by monolayer sorption without interaction among the adsorbate.

The linearized form of Langmuir isotherm equation is as follows [4]:

$$
\frac{1}{q_e} = \frac{1}{Q_0^b} + \frac{1}{bQ_0^bC_e} \quad (4)
$$

where,

- $q_e$ = adsorbate adsorbed per unit weight of adsorbent at equilibrium, mg g$^{-1}$,
- $C_e$ = equilibrium concentration of the adsorbate in solution, mg L$^{-1}$,
- $Q_0^b$ = monolayer adsorption capacity, mg g$^{-1}$,
- $b$ = a constant related to free energy or net enthalpy of adsorption.

When $1/q_e$ was plotted against $1/C_e$, a straight line with slope $1/bQ_0^b$ and intercept $1/Q_0^b$ is obtained (Figure 2-a), which shows that the adsorption of Cu$^{2+}$ by TLP follows the Langmuir isotherm. The Langmuir parameters, $Q_0^b$ and $b$, are calculated from the slope and intercept of the graphs (Figure 2-a) and are given in Table 1.

| Table 1. Langmuir and Freundlich constants for copper ion adsorption |
|-----------------------------------------------|
| **Langmuir parameters** | Adsorption maxima | Binding energy | $R^2$ coef. |
|--------------------------|-------------------|----------------|-------------|
| $Q_0^b$ [mg g$^{-1}$]    | 94.34             | constant $b$ [mg L$^{-1}$]$^{-1}$ | 0.993       |
| **Freundlich parameters** | Adsorption capacity | Adsorption intensity 1/n | $R^2$ coef. |
| $K_F$ [mg g$^{-1}$]     | 2.36              | 1.61           | 0.987       |

The Freundlich isotherm describes the equilibrium of an adsorption system where the adsorption surfaces are heterogeneous. Hence the surface does not assume monolayer characteristics. As compared to the Langmuir model, the energy term $b$ in the Langmuir equation (see Eq 4) varies as a function of surface coverage [4].

The linearized Freundlich equation is as follows:

$$
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)
$$

where $q_e$ is the amount of adsorbate adsorbed per unit weight of adsorbent (mg g$^{-1}$), $C_e$ is the equilibrium concentration of the adsorbate in solution (mg L$^{-1}$), $K_F$ is the relative adsorption capacity constant of the adsorbent (mg g$^{-1}$) and $1/n$ is adsorption intensity.

Plots of Freundlich isotherm ($\log q_e$ against $\log C_e$) would yield a straight line with slope $1/n$ and intercept $\log K_F$. (Figure 2-b). The Freundlich parameters for the adsorption of Cu$^{2+}$ (Table 1) indicate that the adsorption followed both the Freundlich ($R^2 = 0.98$) and the Langmuir isotherms ($R^2 = 0.99$), with the Langmuir isotherm best fits the current experiment.
3.3. Thermodynamic parameters

Figure 3-a depicts the effect of temperatures on Cu\textsuperscript{2+} adsorption carried out in the current study. As shown, higher temperatures enhanced the metal ions adsorption. It can be argued that temperature increases the mobility of ions by contributing additional energy, hence more adsorption. Further, higher temperature may generate a swelling effect so that Cu\textsuperscript{2+} may permeate further into the internal structure of the TLP.

Adsorption processes can be expressed in terms of changes in thermodynamics parameters: Gibbs free energy (\(\Delta G^\circ\)), enthalpy (\(\Delta H^\circ\)) and entropy (\(\Delta S^\circ\)). These parameters are related as follows.

\[
\Delta G^\circ = -RT \ln K_c
\]

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]

where

\(G^\circ = \text{change in free energy, kJ mol}^{-1}\); \(H^\circ = \text{change in enthalpy, kJ mol}^{-1}\); \(S^\circ = \text{change in entropy, J mol}^{-1}K^{-1}\); \(T = \text{absolute temperature, K}\); \(R = \text{gas constant} = 8.314 \times 10^{-3}\); and \(K_c = \text{equilibrium constant}\).
Next, $K_c$ can be defined as:

$$K_c = C_{Ac} C_c$$ \hspace{1cm} (8)

where $C_{Ac}$ and $C_c$ are the equilibrium concentration (mg L$^{-1}$) of the adsorbate, on TLP and in the solution respectively.

Further arrangements of Eqs 5 and 6 would yield the following:

$$\log K_c = \frac{\Delta S^o}{2.303} - \frac{\Delta H^o}{2.303RT}$$ \hspace{1cm} (9)

The adsorption thermodynamic parameters were calculated by plotting $\log K_c$ versus $1/T$ (known as van’t Hoff plot), as shown in Figure 3-b, where the slope and intercept of the plot equal $\Delta H^o/2.303 R$ and $\Delta S^o/2.303 R$, respectively. Hence, the values of $\Delta H^o$ and $\Delta S^o$ were obtained (Table 2).

| Temperature ($^\circ$C) | $K_c$ | $\Delta G$ (kJ mol$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (kJ mol$^{-1}$) |
|-------------------------|------|------------------------|------------------------|------------------------|
| 27                      | 0.94 | -27.84                 | 0.02                    | 0.09                   |
| 30                      | 1.02 | -28.11                 |                        |                        |
| 40                      | 1.13 | -29.04                 |                        |                        |

The positive values of $\Delta H^o$ indicates that adsorption of Cu$^{2+}$ on TLP is endothermic, and thus the adsorption performance would tend to increase with temperature and may involve a chemisorption mechanism [4]. On the other hand, the overall free energy changes, $\Delta G^o$, are negative indicating a spontaneous and thermodynamically feasible process for Cu$^{2+}$ adsorption. The absolute values of $\Delta H^o$ increases with temperature which implies that the spontaneous nature of adsorption of Cu$^{2+}$ is inversely proportional to temperature [4]. The entropy of adsorption, $\Delta S^o$, is positive, suggesting an increase in randomness at the solid-solution interface during the adsorption process.

3.4. Adsorption kinetics

In the present experiment the simple pseudo-first order kinetic model, i.e the Lagergren was employed, and shown in Eq (10) [4]:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_{ad}}{2.303}\right) t$$ \hspace{1cm} (10)

where $k_{ad}$ is the Lagergren rate constant for adsorption (min$^{-1}$), $q_t$ and $q_e$ are the amounts of adsorbate adsorbed (mg g$^{-1}$) at time $t$ and equilibrium time, respectively.

Figure 4 Pseudo-first order kinetic of Lagergren for different temperatures and Ea determination
The plots of Eq 10 were drawn for different temperatures (Fig 4-a) and indicate the applicability of the equation. The values of $k_{ad}$ at room temperature, 30°C and 40°C were calculated from the slope of the linear plots and were found to be: 0.028; 0.036 and 0.049 per min, respectively. The increase in rate constants with temperatures denotes that the rate-limiting step is surface adsorption and the process is endothermic[4]. The adsorption process was also investigated in relation to its activation energy $E_a$, using Arrhenius equation:

$$\ln k_{ad} = \ln A - \frac{E_a}{RT}$$

where $E_a$ the activation energy (kJ mol$^{-1}$), $T$ the temperature in Kelvin, and $R$ is the gas constant = 8.31 kJ mol$^{-1}$ K$^{-1}$. The plot of Eq 11 yields a straight line with slope $-E_a/R$ (Figure 4-b), and the activation energy was found as 127.94 kJ mol$^{-1}$.

4. Conclusion

Dried teak (Tectona grandis sp) leaves were pulverized and subsequently tested as adsorbent for Cu$^{2+}$ adsorption from aqueous solutions. The equilibrium of the adsorption process was reached after approximately 200 min. The maximum adsorption capacity was observed at the following conditions: pH = 6.0; adsorbent sizes: 100-170 mesh, and adsorbent dose: 10 g L$^{-1}$. Langmuir isotherm and Lagergren pseudo first order kinetic were found to be best matched with the experimental data. Calculations of the thermodynamic parameters indicates that the adsorption was endothermic and spontaneous. The activation energy of the adsorption was high i.e.127.94 kJ mol$^{-1}$.

The adsorption experiment was easy and safe to conduct. The utilization of agricultural wastes as adsorbent would show to students that the adsorption is environmentally friendly. The students were able to analyze the experimental data and satisfactorily complete the lab report, indicating that their understanding of the underlying concepts of adsorption: equilibrium, kinetic and thermodynamic improved.

5. References

[1] Martin-Lara M A, Blazquez G, Trujillo M C, Perez A, Calero M 2014 New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone J.Cleaner Production 81 120-129
[2] Munagapati V S, et al. 2010 Biosorption of Cu(II), Cd(II) and Pb(II) by Acacia leucocephala bark powder: Kinetics, equilibrium and thermodynamics Chem.Eng.J. 157 357-365
[3] Vilvanathan S and Shantakumar S 2012 Removal of Ni(II) and Co(II) ions from aqueous solution using teak (Tectona grandis) leaves powder: adsorption kinetics, equilibrium and thermodynamics study Desalin.Water Treat. DOI:10.1080/19443994.2014.989913
[4] Vankar P S, Sarswat R, Sahu R 2012 Biosorption of zinc ions from aqueous solutions onto natural dye waste of Hibiscus rosa sinensis: thermodynamic and kinetic studies Environ. Prog.Sustain. 31(1) 89-99
[5] Ucun H, et al. 2002 Biosorption of chromium (VI) from aqueous solution by coke biomass of Pinus sylvestris Bioresour. Technol. 85 155-158
[6] Azououa N, et al. 2010 Adsorption of cadmium from aqueous solution onto untreated coffee-grounds: Equilibrium, kinetics and thermodynamics. J.Hazard.Mater. 184 126-134
[7] Gashemi M, et al. 2015 Microwave-assisted functionalization of Rosa canina L fruits activated carbon with tetraethylenepentamine and its adsorption behavior towards Ni(II) in aqueous solution: Kinetic, equilibrium and thermodynamic studies Powder Technol. 274 362-371
[8] Piergianni P R 2016 Introductory adsorption laboratory experiment, Paper presented at 2012 ASEE Annual Conference, San Antonio, TX, USA. https://peer.assec.org/21610 (accessed 12 May 2016).
[9] Perić J, Trgo M, Medvidović N V 2004 Removal of zinc, copper and lead by natural zeolite – a comparison of adsorption isotherms Water Res. 38 1893-1899