Adsorption of manganese and zinc in synthetic wastewater by tea waste (TW) as a low cost adsorbent

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Abstract. In this study, tea waste (TW) is investigated as a low cost adsorbent for the treatment of Mn(II) and Zn(II) in synthetic wastewater. Experimental design, the variables are the adsorbent dosage (0.5g, 1.0g, 1.5g, 2.0g, 2.5g and 3.0g) and contact time (20, 40, 60, 80, 100 and 120 minutes). The percentage of heavy metal ions removal in the solution are measured using DR2800 Spectrophotometer. Adsorption Isotherm and Adsorption Kinetic modelling are applied to further prove the correlation of the experimental data obtained for the removal of Mn(II) and Zn(II). The equilibrium data satisfactorily fitted into Langmuir Isotherm model for both Mn(II) and Zn(II) with R² value of 0.9906 and 0.9854, respectively. Based on the result, TW is capable to adsorb more than 90% of both Mn(II) and Zn(II) at optimum dosage of 2g/100ml. The kinetic studies show that the absorption mechanisms satisfied the Pseudo-Second-Order model and have the best equilibrium data with R² value of 0.9998 and 1.0000 for Mn(II) and Zn(II), respectively. The maximum adsorption achieved at 60 minutes for Mn(II) and 80 minutes for Zn(II). Thus, the Langmuir Isotherm and Pseudo-Second-Order Kinetic models proved that TW is capable of being an efficient and effective adsorbent for Mn(II) and Zn(II) removal in synthetic wastewater.

1. Introduction

Hazardous heavy metal pollutants have been generated by anthropogenic activities such as industrial, domestic sewage, agriculture activities and technology production, and illegally released to rivers by irresponsible parties. The industrial processes and productions such as metal plating, Cd-Ni batteries, fertilizer, mining pigmentation, stabilizer and alloy production are increasing due to the development in urban areas. As the result of discharging untreated domestic and industrial waste into the water bodies, the rivers are usually linked to many water quality problems [1].

Adsorption technique is an effective method in treating heavy metals in wastewater. The presence of highly dissolved Mn(II) and Zn(II) concentration in industrial wastewater contribute to the decoloration of water and health problems for long-term exposure to these heavy metals. A few technologies in treating wastewater have been introduced to prevent the negative impacts of heavy metal toxicity. According to [2], adsorption is an effective technique among the processes used for the separation of metal from wastewater if the adsorbent is suitable and adsorbents are properly applied. There are many researchers studied on the production of low cost adsorbent from by-products or wastes such as fruit juice waste, fruit seeds, fruit peels, fruit leaves, eggshell, rice husks, sawdust, sugarcane, corn cobs etc. These by-products and wastes which are abundant, renewable, readily-available and cheaper are found...
to be effective and efficient in degrading heavy metal in wastewater. According to [3], there is increasing research interest in using low cost adsorbent. In this study, tea waste (TW) is investigated as another low cost adsorbent for removal heavy metal ion in synthetic wastewater.

2. Material and Methods
The materials used in this experiment are tea waste (TW), Manganese, Zinc and distilled water.

2.1. Preparation of Adsorbent
Tea waste (TW) collected from university cafeteria as shown in Figure 1 is washed with boiled distilled water for several times to remove any surface impurities as shown in Figure 2 until it turned colourless. The colour of the TW may affect the adsorption process. The TW is oven-dried at 105°C for 24-hours. Later the TW is sieved by mesh 10 (2mm). In order to preserve the TW, it is stored in an air-tight container as shown in Figure 3 to minimize contact with humidity and ready to use as an adsorbent [4]. Six different masses of TW are used in the tests i.e. 0.5g, 1.0g, 1.5g, 2.0g, 2.5g and 3.0g.

2.2. Preparation of Synthetic Wastewater
Two synthetic heavy metals ion solution i.e. Mn(II) and Zn(II) are prepared by mixing those heavy metal stock solutions with distilled water. The volume of metal stock solution depends on the required concentration of solution. To achieve the desired Mn(II) and Zn(II) synthetic wastewater initial concentration, the volume of standard solutions required to dissolve in the distilled water are computed using the following equation:

\[ V_1 = \frac{M_2 \times V_2}{M_1} \]  

(1)

Where \( V_1 \) and \( V_2 \) are the volume of standard solution required and volume of stock solution (ml), respectively and \( M_1 \) and \( M_2 \) are the desired initial concentration and concentration of standard solution (mg/L), respectively.

2.3. Batch Adsorption Test (optimum contact time and optimum TW dosage)
To get the optimum contact time, a test is conducted using 100ml of heavy metal standard solution with 3.0g TW. The mixture is shaken using an orbital shaker at 200rpm at 20, 40, 60, 80, 100 and 120 minutes. After shaking, the supernatant is filtered using Smith filter paper. It is then analyzed using DR2800 Spectrophotometer as to record the adsorption efficiency of the TW waste in removing the heavy metals. Amount of sorption by the TW is calculated as:

\[ \text{Sorption (\%)} = \frac{(C_0 - C_E)}{C_0} \times 100 \]  

(2)
Where \( C_o \) and \( C_e \) are the initial and equilibrium heavy metal concentrations in the solutions (mg/L), respectively [5]. To get the optimum dosage of TW, the experimental set is repeated at TW dosage of 0.5g, 1.0g, 1.5g, 2.0g, 2.5g and 3.0g/100ml, using the obtained optimum contact time as the constant.

3. Result And Discussion
3.1 Effect of Contact Time
It is essential to investigate the effect of contact time required to reach equilibrium for each designing batch adsorption experiment. The longer the contact time or retention, the more adsorption will be achieved. Once the equilibrium level achieved, there will be no further removal of metal ion.

The effect of contact time on TW adsorption of Mn(II) and Zn(II) are determined using initial concentration and adsorbent dosage constant. In this study, the adsorption process of heavy metal is studied for various time duration (20, 40, 60, 80, 100 and 120 minutes) as shown in Figure 4. The adsorption increased with time. It is found that adsorption increased drastically at the beginning of the process and then it remained constant. The equilibrium time is found to be 60 minutes at 3.0g TW with 95.5% of removal Mn(II). For Zn(II), the equilibrium time is found to be 80 minutes at 3.0g TW with 99.5% of removal. Thus, as demonstrated in Figure 1, further prolongation in the contact time has negligible impact towards the adsorption of both Mn(II) and Zn(II).

![Figure 4](image-url) Contact time vs. removal percentage of Mn(II) and Zn (II).
Condition for Mn(II): TW 3.0g/100ml, Mn(II) 2.2mg/L, speed 200rpm.
Condition for Zn(II): TW 3.0g/100ml, Zn(II) 1.98mg/L, speed 200rpm.

The notable increment in the Mn(II) and Zn(II) removal at the initial stage, is also achieved by [2]. The large amount of surface sites available during the adsorbent-adsorbate interactions [6] are the contributing factor to it. However, considering the consistency in the adsorption rate (equilibrium), it may be speculated the active site availability started to reduce as it is fully occupied by the ions during the early stage.

3.2 Effect of Adsorbent Dosage
The results for adsorptive removal of Mn(II) and Zn(II) with respect to TW adsorbent dose are shown in Figure 5. The removal percentage of Mn(II) and Zn(II) increased when the adsorbent increased. The maximum removal of Mn(II) and Zn(II) are 94.7% and 99.5% respectively at 2.0g TW adsorbent.
Figure 5. Dosage of TW vs. removal percentage of Mn(II) and Zn(II).
Condition for Mn(II): contact time 60 minutes, Mn(II) 1.9 mg/L, speed 200 rpm.
Condition for Zn(II): contact time: 80 minutes, Zn(II) 2.12 mg/L, speed 200 rpm.

It is apparent that the removal percent of heavy metals increased with increased due to the greater availability of the exchangeable sites or surface area. This result is also achieved by [7].

3.3 Adsorption Kinetics
Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, characteristic constant of sorption are determined using a Pseudo-first order equation of Lagergren [8] based on solid capacity and Pseudo-second order equation [9] based on solid phase sorption [10]. The Pseudo-first-order (PFO) assumes that the adsorption is controlled by intra-particle diffusion. It is generally expressed as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (3)

where $q_e$ is the equilibrium adsorption capacity (mg/g), $q_t$ is the amount of the solute adsorbed (mg/g) at time, $t$ and $k_1$ is the PFO constant (min$^{-1}$). Whilst, the assumption of the Pseudo-second-order (PSO) is that the adsorption kinetic is dominated by the chemisorption process and generally expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (4)

Where $t$ is the time (minute), $q_t$ is the solute adsorbed at any time (mg/g), $q_e$ is the equilibrium adsorption capacity (mg/g) and $k_2$ is the PSO rate constant (mg g$^{-1}$ min$^{-1}$).

3.3.1 Adsorption Kinetic Results
It is clear from Figure 6(a) and Figure 6(b) that the reaction for Mn(II) and Zn(II) are not likely to be the first order because of the value of $q_e$ (experimental) are not equal to the value of $q_e$ (theoretical), irrespective of the magnitude of the correlation coefficient, while the values of $q_e$ (experimental) and $q_e$ (theoretical) are very close with higher value of correlation coefficient in case second order as shown in Table 1, therefore the adsorption processes followed well the Pseudo-second order kinetics for Mn(II) and Zn(II).
Table 1. Kinetic models constant of Pseudo-first order and Pseudo-second order

| Heavy metals | \( q_e \) (exp)(mg/g) | Pseudo first order | Pseudo second order |
|--------------|----------------------|--------------------|---------------------|
| Mn(II)       | 2.2                  | \( K_1 \) (min\(^{-1}\)) = -0.0127 | \( K_2 \) (mg/g/min) = 0.2745 |
|              |                      | \( q_e \) (mg/g) = 0.0008           | \( q_e \) (mg/g) = 2.1377 |
|              |                      | \( R^2 = 0.5141 \)                  | \( R^2 = 0.9998 \) |
| Zn(II)       | 1.98                 | \( K_1 \) (min\(^{-1}\)) = -0.0046 | \( K_2 \) (mg/g/min) = 0.7804 |
|              |                      | \( q_e \) (mg/g) = 0.0006           | \( q_e \) (mg/g) = 1.9826 |
|              |                      | \( R^2 = 0.6828 \)                  | \( R^2 = 1 \) |

3.4 Adsorption Isotherm

For the optimizing the design of an adsorption system, it is important to establish the most appropriate correlation for the adsorption equilibrium isotherms. Two isotherm models i.e. Langmuir and Freundlich are attempted in this study. In the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm model can be written as follow \cite{11} \cite{12} \cite{13}.

\[
\frac{C_e}{q_e} = \frac{C_0}{Q_0} + \frac{1}{Q_0K} \tag{5}
\]

Where \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)), \( q_e \) the amount absorbed at equilibrium (mg g\(^{-1}\)), \( Q_0 \) and \( K \) is the Langmuir constants related to adsorption capacity and energy of adsorption. The linear plot of \( C_e/q_e \) versus \( C_e \) shows that the adsorption obeys the Langmuir model. \( Q_0 \) and \( K \) are determined from the slope and intercept of the plot. The essential characteristic of Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, \( R_L \), defined by

\[
R_L = \frac{1}{1 + K_0C_e} \tag{6}
\]
Where $K_L$ is Langmuir constant and $C_0$ is the initial concentration (mg/L), $R_L$ values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [14][15].

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface and adsorption sites are distributed logarithmically with respect to adsorption energy, where adsorption process is described in most water treatment process. Freundlich isotherm can be expressed by [11][12][13].

$$\log q_e = \frac{\log C_e}{n} + \log K_f$$

Where $q_e$ is the amount of metal ion absorb at equilibrium per gram of adsorbent (mg g$^{-1}$), $C_e$ the equilibrium concentration of metal ion in the solution (mg L$^{-1}$), $K_f$ and $1/n$ is the Freundlich model constants. Freundlich parameters $K_f$ and $n$, are obtained by plotting log $q_e$ versus log $C_e$. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), linear (1/n = 1) or unfavorable ( 1/n >1) [12].

### 3.4.1 Adsorption Isotherm Results

Table 2, Figure 7(a) and Figure 7(b) confirm that the Langmuir Isotherm represented the equilibrium data by assuming monolayer adsorption occurs [7] for both Mn(II) and Zn(II) adsorption during the adsorbent-adsorbate interactions. In this study, another important finding is that the value of the separation factor, $R_L$, are 0.0629 and 0.0210 ($0 < R_L < 1$), suggesting that both Mn(II) and Zn(II) adsorption are the favourable process.

**Table 2. Isotherm model constant**

| Heavy metals | $C_0$ (exp)(mg/L) | Langmuir Isotherm | Freundlich Isotherm |
|--------------|------------------|-------------------|---------------------|
| Mn(II)       | 1.90             | $K (mg/l) = 7.8409$ | $K_r = 250.149$ |
|              |                  | $Q_0 (mg/g) = 0.1579$ | $n = 0.3388$ |
|              |                  | $R^2 = 0.9906$     | $R^2 = 0.8308$    |
| Zn(II)       | 2.12             | $K (mg/l) = 21.9566$ | $K_r = 76.2079$ |
|              |                  | $Q_0 (mg/g) = 0.2789$ | $n = 0.2789$ |
|              |                  | $R^2 = 0.9854$     | $R^2 = 0.9346$    |
4. Conclusions

The adsorptive capacity of Mn(II) is found to be 0.1579 mg/g (95.5%) whereas the adsorptive capacity of Zn(II) is found to be 0.2789 mg/g (99.5%). Also, the R² Langmuir Isotherm and Pseudo-Second-Order (PSO) Kinetic are 0.9906 and 1.000, respectively, further verify the correlation of the experimental data suggesting domination of the monolayer chemisorption process for both Mn(II) and Zn(II) removal from synthetic wastewater. Thus, the isotherm and kinetic adsorption models proved the capability of TW as an adsorbent for the removal of Mn(II) and Zn(II) from synthetic wastewater.

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