Biosorption of MnO$_4^-$ in aqueous solutions using *Pinus insularis*

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**Abstract.** The batch adsorption capacity of *Pinus insularis* in the removal of Mn$^{2+/7+}$ was 4.51 mg/g which was 90.73% removal. As the initial sorbate concentrations were increased, the amount adsorbed also increased. This is due to the presence of functional groups i.e. –OH, –CH, –COO, –C-OH, –C-H and –COO found in the FTIR results and the SEM results showing rough flat multi-layer surface with small amount of pores of the biosorbent. Elemental analysis also showed presence of counterion Ca$^{2+}$ on the surface of the biosorbent that may undergo ion-exchange with the sorbate. The column adsorption study shows that the exhaustion point reached 60% of the influent value of 2 mg/L. The exhaust times correspond to C/C$_0$ = 0.6 for Mn$^{2+/7+}$ onto *Pinus insularis* at a very low initial concentration of MnO$_4^-$ aqueous solution. The volumes of Mn$^{2+/7+}$ spiked water treated at the breakthrough point was 1.254 mL at initial concentration of 2 mg/L, which was the total volume in the column computed by the breakthrough time multiplied by the flowrate. The study predicted the column breakthrough or S-shaped experimental curves of the adsorption wave front.

1. Introduction

The fate and transport of manganese ions are brought about by soil erosion and volcanic emissions. However, manganese emissions may also come from industries like manufacture of iron and steel alloy, glass, welding works, fireworks, dry-cell batteries, and pesticides, as well as burning of gasoline containing methylcyclopentadienyl manganese tricarbonyl (MMT). If the concentrations of manganese exceeds 0.1 mg/l in water bodies, the dissolved oxygen (DO) is reduced, gives undesirable taste and may affect the central nervous system of living organisms [1]. Most of the known treatment technology of this contaminant i.e. ion exchange are expensive. Thus, adsorption is being considered as an alternative treatment. Only a few adsorbents i.e. zeolites [2], plain and acid-treated alumina [3,4], white rice husk ash [5], pithacelobium dulce carbon [6], maize stalks [7], and steel slag [8] were used yet in treating effluent from industries that contain both cationic and anionic metal ions like MnO$_4^-$. To date, only a few studies on agricultural wastes as biosorbents have been conducted for MnO$_4^-$ and all these study utilize biosorbents that were converted to activated carbon. The objective of the study was to determine the adsorptive capacity of *Pinus insularis* (Pine cone) using both the batch and the column adsorption study with no further treatment done to the biosorbent. The performance of the column bed based on the column breakthrough of cones of *Pinus insularis* was determined using...
simulated continuous adsorption study using Aspen Adsorption® Version 8.4.

2. Methodology

2.1 Preparation of biosorbent
The cones of *Pinus insularis* were collected separately in Chungli, Taiwan. Distilled water was used to wash the cones several times to remove all possible adhering dirt. The cones were then air-dried under room temperature. When all the water was evaporated, the samples were oven-dried at 50°C for 24 to 48 hours. The dried samples were then ground and sieved using 30 mesh screen.

2.2 Characterization of biosorbents
The surface properties were analysed using scanning electron microscopy (SEM, Hitachi S-300N) while the particle size distribution of the sample was obtained using a laser diffraction particle size analyzer (LS™ 13 320, Beckman, USA). The functional groups present on the surface of the samples were found using Fourier transform infrared (FTIR, Perkin Elmer Model 1600) spectroscopy. The concentration of the possible major elements on the surface of the samples was examined using an elemental analyzer (HORIBA 7021H). The Cationic Exchange Capacity (CEC) of the sample was also determined using Bio-Rex 70 analyzer [9].

2.3 Preparation of sorbate
Stock solutions of Mn<sup>2+/7+</sup> with initial concentration of 200 mg/L were prepared by dissolving analytic grade KMnO<sub>4</sub> in 1000 ml of double distilled water. Appropriate infinite dilutions of 50 ml volumes were made from the stock solutions to come up with solutions having initial concentrations (C<sub>0</sub>) of 2, 4, 6, 8, 10, 12, 18, and 20 mg/L of MnO<sub>4</sub><sup>2-</sup>. Instead of using real time effluent, the study used simulated a (omit) sorbate solution ranging from the maximum and minimum possible concentrations that may be generated from industrial sources [10].

2.4 Equilibrium studies
The experiments on batch adsorption MnO<sub>4</sub><sup>-</sup> solutions were done in 50-mL plastic bottles on an orbital shaking incubator at 180 rpm until equilibrium was reached. The temperature used was the room temperature. The equilibrium time of 24 h was chosen [9] as compared to 48 h [2] and 8 h [5] conducted by other studies. A preliminary study was conducted by the author and showed that at 24 h the biosorbent had already reached point of saturation. 0.2 g adsorbent with 50 ml of aqueous sorbate solutions of known concentration in a series of conical plastic containers were used at pH adjusted to 5.0 ± 0.1 using 0.1 M HCl or 0.1 M NaOH aqueous solution. After shaking, the solutions were settled for few minutes and then filtered using 0.45 µm Whatmann filter to separate the filtrate from the adsorbent. Then at time t = 0 and at equilibrium, concentration of the total manganese ions were determined using atomic absorption spectrophotometer (Avata, AAS GBC) at maximum wavelength of 640 nm to represent the amount of contaminants adsorbed on the biosorbents. The calibration curve was then used to compute for the concentrations. The adsorption calibration curve was constructed composed of a blank of five standards from Merck (Germany). External standard reference material for total Mn ions in water was used to maintain accuracy and precision of the sorbate measurement.

2.5 Isotherm models
The \( q_e \) (mg/g), which represents the amount of total Mn ions adsorbed onto the pine cone at time t, was calculated by the following mass balance relationship:

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

(1)

where \( C_0 \) and \( C_e \) were the initial and equilibrium liquid phase concentrations of sorbate, respectively (mg/L), \( V \) the volume of the solution (L), and \( W \) the weight of the biosorbent used (g). The results
were fit into linearized Langmuir (equation (2)), Freundlich (equation (3)) and Temkin (equation (4)) isotherm models [5] to compare which would have the best fit and to determine the maximum adsorption capacity of *Pinus insularis*.

\[
\frac{q_{eq}}{C_{eq}} = b \frac{q_{max}}{b} - b \frac{q_{eq}}{C_{eq}}
\]  

(2)

\[
\log q_{eq} = n \log c_{eq} + \log K_F
\]  

(3)

\[
q_{eq} = \frac{RT}{b_f} \ln c_{eq} + \frac{RT}{b_f} \ln A_T
\]  

(4)

Here \(q_{max}\) is the maximum adsorption capacity of the bed (mg/g), \(c_0\) is the initial sorbate concentration (mg/L), \(c_{eq}\) is the equilibrium concentration of adsorbate (mg/L), \(q_{eq}\) is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), \(n\) is the adsorption intensity, \(K_F\) is Freundlich isotherm constant, \(R\) is the universal gas constant (8.314 J/mol-K), \(T\) is the absolute temperature (K), \(b_T\) is the Temkin isotherm constant, and \(A_T\) is the Temkin isotherm equilibrium binding constant (L/mg).

### 2.6 Preparation of sorbate of continuous adsorption

Continuous adsorption of MnO\(_4\) onto *Pinus insularis* used in batch adsorption was simulated using Aspen Adsorption® 8.4. Preparation of the sorbate was the same as how it was done in batch adsorption.

### 2.7 Physical and chemical properties of sorbate solution used in the continuous adsorption

The physical properties of these electrolytes in combination with water were provided by Aspen Properties® and the property method used was ELECNRTL (Electrolyte Non-random Two-Liquid) used for both very low and very high concentration in aqueous systems.

### 2.8 Bed configuration used in continuous adsorption

The following parameters were used for the column study: (1) inter and intraparticle diameter and particle size of the biosorbent using the results from particle size distribution analysis; (2) adsorption capacity recovery of contaminant (Q) using the linearized form of Langmuir isotherm; (3) amount of biosorbent dosage related to column bed depth or height (H\(_b\)); and, (4) influent flow rate (F). Total pore of the biosorbent (\(\varepsilon_1\)) was computed from the interparticle size (cm\(^3\)/g) and bulk density (cm\(^3\)/g) while the micro pore (\(\varepsilon_p\)) was computed from the intraparticle size (cm\(^3\)/g). The set of equations within the layer of the bed were specified in the “Configure Block/Stream” window. The General Tab was selected and the discretization method and the number of nodes were set. The Upwind Differencing Scheme (UDS) 1 was used as the discretization method.

### 2.9 Simulation of the continuous adsorption

The product concentration was initially set to zero in order to determine the breakthrough time at the breakthrough concentration, \(C_b\). Breakthrough concentration was set to five percent of its concentration in the feed (\(C_o\)). The study predicted the column breakthrough obtained by plotting throughput volume (\(V_t\)) at any time (t) versus effluent concentration (C). The residence time that may be derived from the curve was based on the flow rate (F) and the mass transfer coefficients (MTC) of the adsorption system. Concentrations at the breakthrough point (at \(C_b = 0.5C_o\)) of the process effluent were recorded for every simulation. The dynamic equilibrium loading, \(q_{eq}\) was determined by dividing the amount of sorbate adsorbed up to the breakpoint by the quantity of biomass used in the packed bed. The total volume used was computed by multiplying the breakthrough time and multiplied by the
flowrate.

3. Results and discussion

3.1 Preparation of biosorbents

Agricultural wastes when subjected to protonation like drying at high temperature (50°C) for 24 to 48 hours without converting to char forms functional groups i.e. acetamido groups, carbonyl, phenolic, structural polysaccharides, amide, amino, sulphhydryl carboxyl groups alcohols and esters [11]. These functional groups serve as the binding sites to the contaminant with strong affinity to Mn$^{+2/+7}$ in aqueous solution.

3.2 Characterization of biosorbents

The surface properties of *Pinus insularis* samples were determined using scanning electron microscopy (SEM). Figure 1 shows the samples of *Pinus insularis* with rough flat multi-layer surface with small amount of pores that can initiate adsorption of MnO$_4^-$ [9].

![Figure 1](image1.png)

**Figure 1.** Surface properties using scanning electron microscopy (SEM) of the *Pinus insularis* samples.

The Fourier transform infrared (FTIR) spectroscopy analysis of *Pinus insularis* is shown in figure 2 indicating the available functional groups on its surface that provide binding sites and strong affinity to MnO$_4^-$ in aqueous solution. These functional groups were produced upon protonation of cellulose, hemicelluloses, xylose and lignin present on the surface of the agricultural wastes when water molecules were removed during drying. The FTIR spectroscopy analyses indicate that *Pinus insularis* results have 3727.73 cm$^{-1}$ for –OH, 2982.37 cm$^{-1}$ for –CH, 2317.05 cm$^{-1}$, 1792.51 cm$^{-1}$, and 1518.67 cm$^{-1}$ all for –COO, 1184.08 cm$^{-1}$ for carboxyl and hydroxyl C–OH, and 695.212 cm$^{-1}$ for C–H.

![Figure 2](image2.png)

**Figure 2.** Fourier transform infrared (FTIR) spectroscopy analysis of *Pinus insularis*. 
3.3 Equilibrium studies
Figure 3 shows the equilibrium study of MnO$_4^-$ with *Pinus insularis* showing an adsorptive capacity of 4.51 mg/g which is 90.73% removal of the contaminant. As the initial concentration of total Mn ions was increased, the amount adsorbed also increased.

![Graph showing equilibrium studies](image)

**Figure 3.** Results of batch adsorption equilibrium studies of MnO$_4^-$ onto *Pinus insularis*.

It is due to the available binding sites on the surface of *Pinus insularis* which contains Ca$^{2+}$ that may serve as counterion as shown in the elemental analysis of the sample and the properties of Ca$^{2+}$. Table 1 indicates the comparison of different properties of the sorbate and the counterion.

| Metal/Cation | Ionic Radius (Å) | Hydrated Ionic Radius (Å) | Ionic Pauling’s Electronegativity |
|--------------|------------------|---------------------------|----------------------------------|
| Mn$^{2+/7+}$ | 0.46             | 3.00                      | 1.55                             |
| Ca$^{2+}$    | 1.06             | 2.70                      | 1.00                             |

As the ionic radius of the sorbate ion gets smaller as compared to that of the counterions present on the surface of the biosorbent, the greater is the adsorption because during ion exchange, more ions of the contaminant can fit into the pores of biosorbent initially occupied by the counterions. Comparing the ionic radius of Mn$^{2+/7+}$, it is smaller than that of the ionic radii of counterion Ca$^{2+}$ present in *Pinus insularis*. [12]. Ion exchange may also likely to occur due to the Cationic Exchange Capacity (CEC in meq per 100g) of *Pinus insularis* which is 43 meq per 100 g. Another property that may explain the adsorptive capacity of the biosorbents is the hydrated radius that refers to the size of the water molecule in comparison to normally stabilizing cations that causes the physical enlargement or swelling of the adsorbing medium that then causes decrease in permeability. Since the hydration of Mn$^{2+/7+}$ is smaller than that of Ca$^{2+}$, ion exchange takes place easier and adsorption will then be more probable [12]. The electronegativity of Mn$^{2+/7+}$ is also higher than that of Ca$^{2+}$ thus it was adsorbed readily by the biosorbent since a more electronegative ion is more strongly attracted to the surface of *Pinus insularis* [13]. The higher the precipitation value of the ions, the higher the amount of the formed colloids adsorbed [14]. MnO$_4^-$ has high coagulating value and thus can be adsorbed easily. Point of saturation was reached when the entire surface of the biosorbents were covered. The peak concentration shows equilibrium was already reached [2,15].
3.4 Isotherm study

The data in the batch adsorption show that for Mn$^{2+/7+}$ removed by the *Pinus insularis* best fit in the linearized form of Langmuir isotherm shown in equation (5)

$$\frac{q_{eq}}{C_{eq}} = b_L q_{max} - b_L q_{eq}$$  \hspace{1cm} (5)

where $q_{eq}$ is the equilibrium concentration of the heavy metal per unit mass of adsorbent (m/g), $q_{max}$ is the maximum adsorption capacity of the biosorbent (mg/g), $C_{eq}$ is the equilibrium concentration of adsorbate (mg/L), $b_L$ is a Langmuir isotherm constant (L/mg), and $q_{eq}$ is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), agreed with the resulting $q_{max}$ of the biosorbents. The $q_{max}$ of *Pinus insularis* is 4.51 mg/g and the $R^2$ is 0.995. For the Freundlich isotherm model, $R^2$ is 0.938, the adsorption intensity $n$ is 1.803 and the $K_F$ is 1.499. For the Temkin isotherm model, $b_T$ constant is 4.834 while the Temkin isotherm equilibrium binding constant, $A_T$ in L/mg is 1.276.

3.5 Continuous adsorption

Batch adsorption data for Mn$^{2+/7+}$ adsorbed onto *Pinus insularis* system, were correlated to the parameters required in the Aspen Adsorption® 8.4. The amount of biosorbent dosage was related to column bed depth or height ($H_b$). Surface area, average particle diameter ($r_p$); bulk density ($\rho_L$), inter ($\varepsilon_i$) and intraparticle ($\varepsilon_p$) diameter of the biosorbent based from the characterization of powdered biosorbents were used in the computation of the total pore of the biosorbent and the micro pore sizes of the biosorbent, respectively while the elemental analysis was used to determine the concentration of the counterion present on the surface of the biosorbent. The total resin capacity was assumed to be the summation of the capacities of the adsorbent for each metal in a multi-metal solution.

The contaminant concentrations at the breakthrough point ($C_b$) of the process effluent were recorded for every simulation run. From the breakthrough plots e.g. shown in figure 4 generated using Aspen Adsorption® 8.4, breakthrough concentrations and breakthrough times were determined. The breakthrough profile obtained was S-shaped curve that depicts the concentration history during the adsorption process. The point when the contaminant in solution can no longer be adsorbed by the adsorbent is called the breakpoint. The total volume used was computed by determining the breakthrough time and multiplying it to the flowrate.

![Breakthrough](image_url)

**Figure 4.** Sample breakthrough curve for 10 mg/L initial Mn$^{2+/7+}$ concentration adsorption onto *Pinus insularis* using Aspen Adsorption® 8.4.

As the initial concentration increase, the more the slope of the breakthrough curve gets steeper recording a shorter breakthrough time [16]. This shows that the initial sorbate concentration is directly
proportional with the equilibrium loading. In the column study, the initial sorbate is also directly proportional with time. The breakthrough times for Mn$^{2+/7+}$ adsorbed onto *Pinus insularis* were found to be 1600s, 650s, 240s, 23.5s, 19s, 17s, 14s and 13s, for initial concentrations (Co) of 2, 4, 6, 8, 10, 12, 18, and 20 mg/L of total Mn ions, indicating a very rapid time to reach the system breakthrough. The point where the effluent concentration reaches 60% of the influent value (2 mg/L) is called the point of column exhaustion. The exhaustion time correspond to $C/C_0 = 0.6$ for this system. The volumes of Mn$^{2+/7+}$ spiked water treated at the breakthrough point was 1.254 mL, which is the total volume in the column computed by the breakthrough time multiplied by the flowrate. The concentration in the effluent must be reduced so that it does not exceed allowable limit of breakthrough concentration. The study predicted the column breakthrough or S-shaped experimental curves of the adsorption wave front.

4. Conclusion
The adsorption capacity of *Pinus insularis* in adsorbing Mn$^{2+/7+}$ was determined as 4.51 mg/g, 90.73% removal. Increasing the initial sorbate concentrations also increased the amount adsorbed. The column exhaustion point reached 60% of the influent value of 2 mg/L of MnO$\text{}_4$ aqueous solution. The exhaust times correspond to $C/C_0 = 0.6$ for this system. The volume of Mn$^{2+/7+}$ spiked water treated at the breakthrough point was 1.254 mL, which is the total volume in the column computed by the breakthrough time multiplied by the flowrate. The study predicted the column breakthrough or S-shaped experimental curves of the adsorption wave front.

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