Summary

$Ni^{2+}(aq)$, $Pb^{2+}(aq)$, $Cu^{2+}(aq)$, $Mn^{2+}(aq)$, $Hg^{2+}(aq)$, $Zn^{2+}(aq)$ and $Fe^{3+}(aq)$, as well as used tea leaves of Iron Goddess, Red Tea, Jasmine and Pu-erh, are used to investigate the removal of aqueous heavy metal ions, $M^{n+}(aq)$, by used tea leaves.

The precipitation method is used to determine the percentage absorption (P%) of M^{n+} (aq) and the amount of $M^{n+}(aq)$ being absorbed by used tea leaves for 2 days:

$$P\% = \frac{M1 - M2}{M1} \times 100\%$$

where M1 and M2 are the mass of precipitate produced from $M^{n+}(aq)$ in used tea solution without tea leaves and in the presence of tea leaves, respectively. This method avoids knowing the exact formula of the precipitate and disregards of the adsorption of water-soluble tea substances by the precipitate, provided that the formula of the precipitate does not change during the precipitation and the amount of the water-soluble tea substance adsorbed by the precipitate is directly proportional to the mass of precipitate.

The amount of metal ions being absorbed per unit mass of used tea leaves (A, unit: mol / g) can then be calculated using the following formula:

$$\text{A} = \frac{CV}{1000m} \times P\%$$

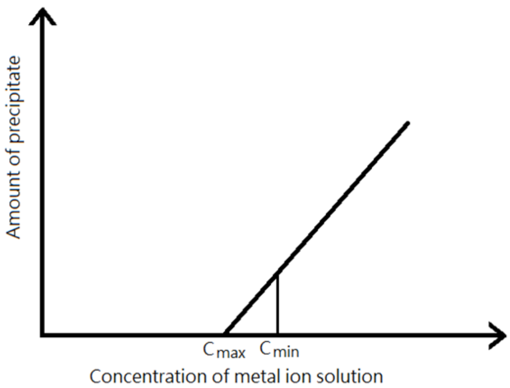
Where C: Molarity of the heavy metal ion solution (mol / dm^3)

V: Volume of the heavy metal ion solution (cm^3)

m: Mass of dry used tea leaves

In order to investigate and compare the rate of each type of heavy metal ions adsorbed by each type of used tea leaves, the amount of $M^{n+}(aq)$ in a metal ion solution of known volume (V) and known concentration, soaked in used tea leaves of known dry mass, being absorbed within a certain period of time is determined experimentally. First, experiments are carried out to find out **the minimum concentration of a heavy metal ion solution for the appearance of precipitate (C_{min}, unit: mol / dm^3)** (or the appearance of colour in the solution) and **the maximum concentration of the solution for no precipitation (C_{max}, unit: mol / dm^3)** (or the solution turns colourless again) when a precipitating reagent (or a complexing reagent for the formation of coloured complex with $M^{n+}(aq)$) is added to the solution (Fig. 1). Then, **the soaking time (t) for no visible change** is determined when **dry used tea leaves of known mass (m, unit: g) soaks in a heavy metal ion solution of same volume, V, and concentration, C_{min}.**

Fig.1. A graph for showing the appearance of precipitate as the concentration of the metal ion solution increases. C_{max} is the concentration below which there would be no precipitation with the precipitation reagent. C_{min} is the concentration at which the precipitate starts to be visible.



The following formula is used for estimating the average rate of the absorption of metal ions per unit mass of used tea leaves (R, unit: mol/g•min):

$$R = \frac{(C_{min} - C_{max})(V \div 1000)}{mt}$$

The soaking time (t) will be more accurate if the testing reagent is added at shorter time intervals. By the concept of differentiation, the smaller is the difference between Cmax and Cmin, the more accurate will be the value of R (Fig. 2). **This innovative method can be applied for determining the rate of a reaction in school laboratories where advanced instrument, such as GCMS, is not available.**

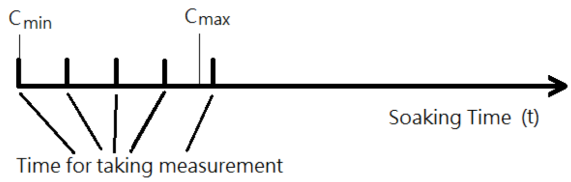


Fig. 2. A diagram for showing the concept of getting the soaking time (t) for no visible change when a testing reagent is added to a metal ion solution of concentration of C_{min} at regular time intervals.

The amount of metal ions being absorbed per unit mass of used tea leaves in 2 days can be regarded as a measure for the absorption capacity of used tea leaves. Our experimental results showed that **the used tea leaves could absorb all the seven types of heavy metal ions but to different extents**. Pb^{2+}(aq) is relatively poorly absorbed while Zn^{2+}(aq), Ni^{2+}(aq) and Hg^{2+}(aq) are relatively effectively absorbed by used tea leaves The used Jasmine and Red Tea tea leaves are the best for absorbing effectively, on average, the seven types of heavy metal ions whereas Iron Goddess is the worst one. **Different types of used tea leaves may have a quite large difference in absorption capacity for the same type of metal ions**. For example, Pu-erh can absorb Cu^{2+}(aq) 5.7 times more than Iron Goddess can do. On the other hand, **same type of used tea leaves may have different absorption capacities for different types of heavy metal ions.** For example, used Red Tea tea leaves can absorb about 12 times more Fe^{3+}(aq) than Pb^{2+}(aq).

The average rate of the absorption of metal ions per unit mass of used tea leaves can be considered as a measure for the absorption ability for M^{n+}(aq). Our experimental results have shown that Zn^{2+a}(aq) can be absorbed relatively fast whereas Fe^{3+}(aq) are absorbed relatively slowly by most types of used tea leaves. In general, Red Tea tea leaves absorb fastest among the four types of used tea leaves for most of the heavy metal ions. **Same type of used tea leaves may have a large difference in the absorption ability for different types of heavy metal ions**. For example, used Iron Goddess tea leaves absorb zinc ions about 96 times faster than iron(III) ions. On the other hand, **different types of used tea leaves also may differ greatly in the absorption ability for the same type of heavy metal ions**. For example, Pu-erh absorbs about 52 times faster than Jasmine for Ni^{2+}(aq).

It has been suggested that metal removal by waste tea leaves is a typical sorption of metals, involving metabolically inert bio-mass, where metal removal from solution is purely due to the chemical and physical sorption, which reaches equilibrium relatively fast during the initial 0-30 min followed by slower diffusion into the sorbent particles. The absorption mechanism may be divided into three stages (Fig. 3):

(1) The fast adsorption of the heavy metal ions on the leaf surface.

(2) The slow diffusion of heavy metal ions into the interior of the tea leaf.

(3) The chemical absorption of the metal ions by the functional groups of the molecules of the tea leaf.

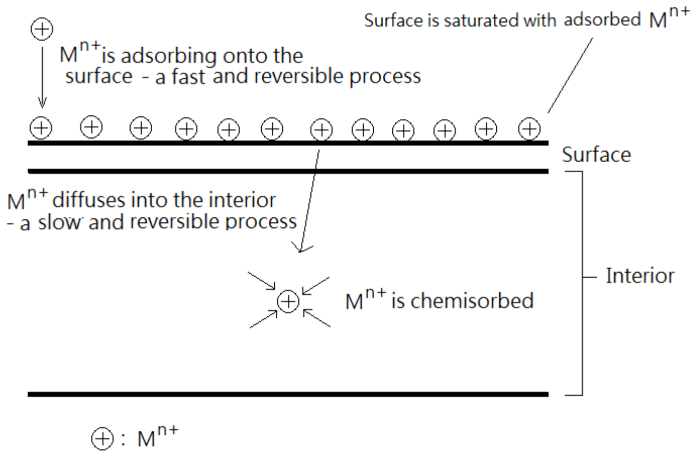


Fig. 3. A schematic diagram to show the three stages in the mechanism for the aqueous metal ions being absorbed into a tea leaf.

The mechanism can explain our experimental results. **Some used tea leaves can absorb a type of heavy metal ions fast but little.** For example, used Iron Goddess tea leaves can absorb Cu^{2+}(aq) fast but relatively little. This may be due to the fact that the diffusion rate of adsorbed copper(II) ions from the surface to the interior of the leaf is quite fast but the absorption sites for them is relatively few in an Iron Goddess leaf. On the other hand, **some used tea leaves can absorb a type of heavy metal ions slowly but quite much**. For example, used Jasmine tea leaves can absorb Ni^{2+}(aq) slowly but relatively quite much . This may be due to the fact that the diffusion rate of adsorbed nickel(II) ions from the surface to the interior of the leaf is quite slow but the absorption sites for them is relatively abundant in a Jasmine leaf.

In general, the rate of reaction usually depends on the concentration of a reactant. However, a research showed that adsorption at low concentration of metal ions was independent of initial concentration of metal ions. The reason may be that the active sites on the surface of used tea leaves for adsorbing metal ions is saturated with the metal ions even at low concentrations of metal ions. The followed processes of the diffusion of the adsorbed metal ions into the sorbent particles and chemisorption by the functional groups are slow and rate-determining. Therefore, in our experimental conditions, although the concentrations of the metal ions were not the same, the rate of absorption would not be affected by the difference in the initial concentrations of the metal ions in comparison.

Heavy metals in wastewater are usually in trace amounts (1 mg/l to 100 mg/l) and are usually present in neutral to acidic pH values. The most common method for removing heavy metal ions in waste water is hydroxide precipitation. However, although the solubilities of the metal hydroxides are usually very low, the concentrations of some metal ions such as Zn^{2+} and Pb^{2+} are still about 0.1–10 mg/dm^3 (10^{-5}M –10^{-3}M) after the treatment of hydroxide precipitation. The heavy metal ions at such low concentrations may still be harmful to the aquatic lives. Our experimental results have shown that **the used tea leaves are able to quickly absorb heavy metal ions at very low concentrations**. 100 g used tea leaves may absorb almost completely most metal ions in solutions of volume 1 dm^3 and concentration 10^{-4}M within 30 seconds and may be able to clean up, in general, over 300 litres of waste water with that concentration of metal ions. Therefore, **used tea leaves have a great potential in further lowering the concentrations of heavy metal ions in waste water after hydroxide precipitation**.