Removal of lead from aqueous solutions by spent tea leaves

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Spent tea leaves from black and green tea were assessed for their potential to remove lead (II) from contaminated waters. Batch adsorption experiments made at temperatures between 5 and 40 °C and lead ion concentrations between 0.01 and 2 g/L showed that removal efficiencies higher than 95% can easily be achieved. The results were only marginally affected by the type of tea waste. At low lead loading the adsorption equilibrium was well described by the Langmuir equation, with a maximum adsorption capacity of 85–100 mg/g.
A comparison with other adsorbents provided the following order for lead removal efficiency: black tea, coffee grounds > green tea > Fuller's earth > activated carbon.

1. Introduction

After water, tea is the most widely consumed beverage in the world, as attested by the over 3,500,000 tons of tea leaves produced annually (FAO, 2009). Tea beverages are typically available as green, black or Oolong tea, depending on the way of manufacturing (Ho et al., 2008). Black tea, made from the mild oxidation of tea leaves, amounts to around 78% of the whole production, followed by green tea (20%) and Oolong tea (2%). All of them, however, are obtained from the same basic tea leaves (*Camellia sinensis*) which, once the beverage has been brewed, become a waste that must be disposed of. Like other biomass residues, tea wastes represent an unused resource and pose increasing disposal problems (Arvanitoyannis and Varzakas, 2008). For these reasons, strategies are being investigated to evaluate their possible use as an energy source or in other value-added applications (Laufenberg et al., 2003).
Biosorption of heavy metals or other pollutants from contaminated waters is a relatively new and promising area of exploitation of biomass wastes (Bailey et al., 1999). Although biosorption is a cheap and environmentally safe alternative to the use of traditional adsorbents, the suitability of a given biomass for this application needs a careful evaluation. In particular, there appears to be a large variability in the rate and degree of adsorption of a species onto a waste biomass, which could limit its usefulness (Demirbas, 2008).
To gain further insight into the potential of tea wastes as heavy metal biosorbents we have performed a preliminary study on the adsorption behaviour of lead on spent leaves of black and green tea. The adsorption characteristics of the two wastes were compared with those of coffee grounds and two commonly used adsorbents: activated carbon and Fuller's earth.

2. Experimental

2.1 Materials

Spent black and green tea leaves were used for the experiments. Soluble and coloured components were removed from the leaves by repeated washing with boiling water until the filtrate was virtually colourless. Then the solid was washed with distilled water and oven dried at 60 °C for 24 h. The dried leaves were ground and sieved to particles <500 μm which were stored in polyethylene bags until use.

Lead (II) chloride, with a purity >98%, was obtained from Sigma-Aldrich (Milano, Italy). Granular activated carbon (8-mm pellets) and Fuller's earth (powdered form) were from Sigma-Aldrich (Milano, Italy). All other chemicals were of analytical grade and used without further purification.

2.2 Methods

2.2.1. Equilibrium studies

Batch adsorption experiments were carried out in 50-mL screw-top pyrex flasks. The flasks were placed in a water bath thermostated at the required temperature (± 0.05 °C) and magnetically stirred. In a typical experiment, about 0.2 g of dried leaves were contacted with 40 mL of an aqueous solution of lead chloride at pH 5.5. Preliminary runs showed that about 20 h were needed to reach equilibrium. Accordingly, after this time the stirring was stopped and a sample of the solid-liquid suspension was taken. The suspension was filtered two times on filter paper and the liquid was analysed for lead content. The temperature was varied between 5 and 40 °C, the initial lead concentration between 0.01 and 2 g/L and the solid to liquid ratio between 1 and 10 g/L.

2.2.2. Comparison of adsorbents

In these experiments about 0.5 g of the adsorbent were contacted with 50 mL of an aqueous solution at 0.1 g/L lead concentration. The contact time was set at 2 h and the temperature at 25 or 40 °C. In addition to black and green tea leaves, the following adsorbent materials were used: coffee grounds, activated carbon and Fuller's earth.

2.2.3. Analytical methods

Lead ion concentration in the aqueous solutions was determined colorimetrically by a standard test (Nanocolor® Lead 5, Macherey–Nagel GmbH, Germany) based on the reaction of Pb (II) with 4-(pyridyl-2-azo)-resorcinol.

3. Results and Discussion

3.1 Adsorption equilibrium

The amount of lead adsorbed at equilibrium, q^* (mg/g), was calculated by:

$$q^* = \frac{V_L}{w}\left(c_0 - c^*\right) \qquad (1)$$

where c_0 and c^* (mg/L) are the liquid-phase concentrations of lead at initial and equilibrium, respectively, V_L (L) is the volume of the solution and w (g) is the dry mass of adsorbent. Figure 1 shows the results obtained for lead adsorption on green tea waste at 20 °C.

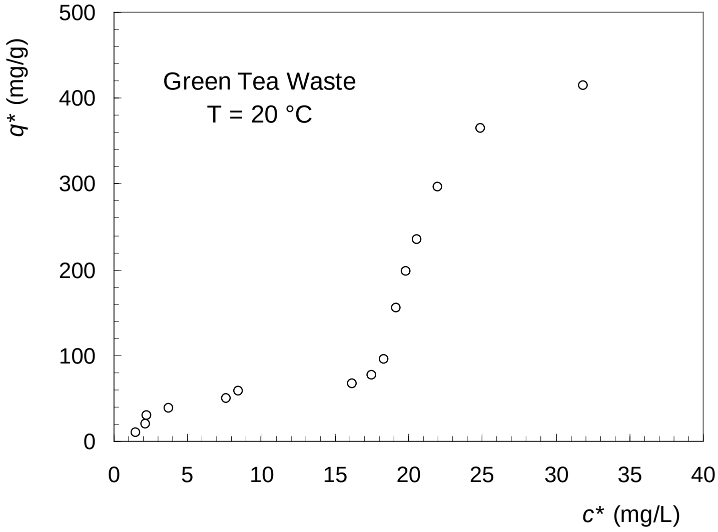

Figure 1 – Adsorption isotherm of Pb (II) on green tea waste.

Similar trends were observed at other temperatures and for black tea. Data points in the figure indicate the occurrence of multilayer adsorption, with a first-layer adsorption capacity of the order of 80–100 mg/g and the second close to 450–500 mg/g. These isotherms are very similar to those reported by Andini et al. (2006), who investigated the adsorption of Pb (II) and Cd (II) onto organophilic bentonite (tetraethylammonium bentonite). The behaviour evidenced in Figure 1 suggests that at low solute concentration moderate interactions are generated between lead ions and tea waste. On proceeding of adsorption, adsorbent-adsorbate interactions increase and promote cooperatively lead loading on the solid.
Relevant to practical applications, however, is the low Pb concentration range, being the solutions to be treated generally highly diluted in lead. We therefore investigated more closely the adsorption properties of tea wastes at low initial concentrations (c_0 < 500 ppm). Under these conditions a removal efficiency of 96.7% (± 2.3%) was obtained. The isothermal data were found to be well described by the Langmuir equation:

$$\frac{q^*}{q_m} = \frac{K_L c^*}{1 + K_L c^*} \tag{2}$$

where q_m is the maximum adsorption capacity and K_L is the adsorption equilibrium constant. These parameters were evaluated by least-square analysis. An illustrative example of the results is shown in Figure 2, whereas the estimates of q_m and K_L are listed in Table 1.
It can be noted that, under the experimental conditions explored, black tea waste exhibited a slightly higher maximum adsorption capacity than green tea (115.4 mg/g against 83.8 mg/g).

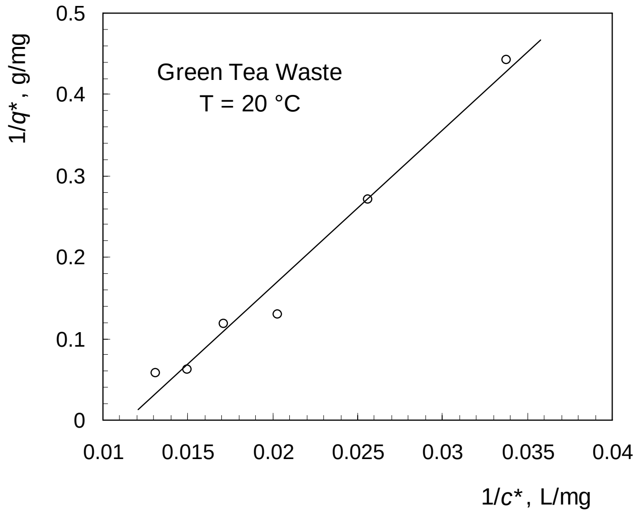

Figure 2 – Linearized Langmuir plot for Pb (II) adsorption on green tea waste.

The average adsorption equilibrium constant was 0.167 L/mg for black tea and 0.211 L/mg for green tea. Overall, however, the two materials had very similar performance in terms of lead adsorption capacity. These results are in substantial agreement with earlier studies on the adsorption of heavy metals (Cd, Cu, Ni and Pb) on tea wastes (Mahvi et al., 2005; Amarasinghe and Williams, 2007; Sabrina and Hasmah, 2008).
The ability of a waste material to bind lead or, more generally, heavy metal ions is the result of a variety of mechanisms, including chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation and surface adsorption (Demirbas, 2008).
In order to understand how lead is removed by the tea waste, it is essential to identify the functional groups responsible for metal binding. Although specific studies on this type of waste are lacking, charged and polar functional groups on the protein surface and phenolic compounds are believed to be primarily involved in metal removal (Basso et al., 2002; Pagnanelli et al., 2003). These groups have the ability to bind heavy metals by the replacement of hydrogen ions for metal ions or by donation of an electron pair to form metal complexes (Ofomajaa and Ho, 2007; Demirbas, 2008).

Table 1– Langmuir parameters for lead adsorption on black and green tea wastes.

Waste material	T (°C)	Δc_0 (mg/L)	q_m (mg/g)	K_L (L/mg)
Black tea	25	70 – 351	129.9	0.112
	40	137 – 342	101.0	0.223
Green tea	20	149 – 400	86.2	0.227
	30	215 – 360	82.0	0.160
	40	141 – 358	83.3	0.245

3.2 Comparison of adsorbents

To quantify the performance of the various adsorbents we evaluated the percent lead removal efficiency as:

$$R\% = \frac{c_0 - c_f}{c_0} \cdot 100 \qquad (3)$$

where c_0 and c_f (mg/L) are the liquid-phase concentrations of lead at time 0 and after 2-h contact. The results are presented in Table 2. Since the materials had different moisture contents, we also calculated the amount of lead (mg) adsorbed per g of dry solid (q_S), obtaining the results shown in Figure 3.

Table 2 – Lead removal efficiency (R%) and moisture content (U %) of tea wastes and other adsorbents.

Waste material	*U* %	*R*%	
		T = 25 °C	*T* = 40 °C
Black tea waste	11.6	98.4	99.3
Green tea waste	7.68	98.0	98.0
Coffee grounds	10.95	99.0	99.0
Activated carbon	2.18	99.3	97.9
Fuller's earth	2.94	99.4	99.4

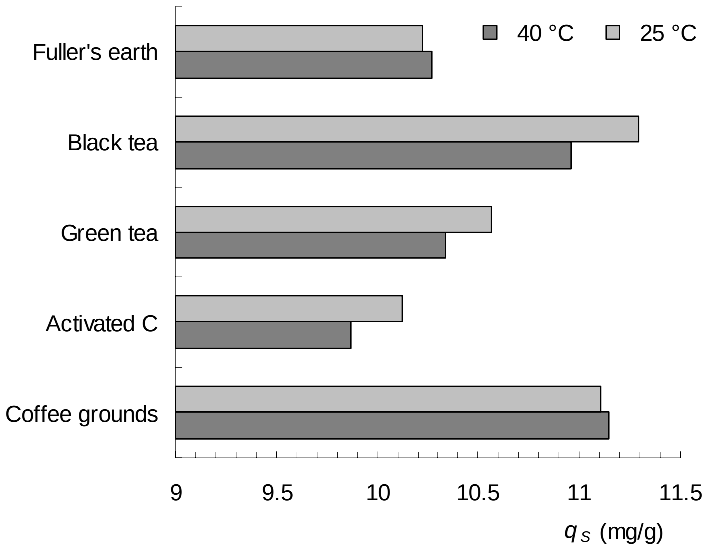

Figure 3 – Amount of Pb (II) adsorbed per g of dry tea wastes or other materials.

Examination of the data in Figure 3 gives the following order of lead removal efficiency: black tea waste, coffee grounds > green tea waste > Fuller's earth > activated carbon. Black and green tea wastes were, on average, more efficient than traditional adsorbents (activated carbon and Fuller's earth) and not too different from coffee grounds. In particular, at 25 °C the amount of lead removed per dry weight of adsorbent was 11.3 and 10.6 mg/g, respectively, for black tea waste and green tea waste.

These results clearly support the possibility of using spent tea leaves for the removal of lead and, possibly, of other heavy metals from contaminated waters. In addition to having a high adsorption capacity, they do not require any pretreatment or activation. Their use as an adsorbent for heavy metal ions can therefore be expected to be economically and technically feasible.

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