Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater

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Abstract

Adsorption of copper and lead ions onto tea waste from aqueous solutions was studied to enable comparison with alternative commonly available absorbents. Batch experiments were conducted to determine the factors affecting adsorption and kinetics of the process. Fixed bed column experiments were performed to study practical applicability and breakthrough curves were obtained. Tea waste is capable of binding appreciable amounts of Pb and Cu from aqueous solutions. The adsorption capacity was highest at solution pH range 5–6. The adsorbent to solution ratio and the metal ion concentration in the solution affect the degree of metal ion removal. The equilibrium data were satisfactorily fitted to Langmuir and Freundlich isotherms. Highest metal uptake of 48 and 65 mg/g were observed for Cu and Pb, respectively. Pb showed higher affinity and adsorption rate compared to Cu under all the experimental conditions. Kinetic studies revealed that Pb and Cu uptake was fast with 90% or more of the adsorption occurring within first 15–20 min of contact time. The kinetic data fits to pseudo second order model with correlation coefficients greater than 0.999. Increase in the total adsorption capacity was observed when both Cu and Pb ions are present in the solution. Higher adsorption rate and the capacity were observed for smaller adsorbent particles. Tea waste is a better adsorbent compared to number of alternative low cost adsorbents reported in literature.
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1. Introduction

Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a world wide environmental problem. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Mining, electroplating, metal processing, textile and battery manufacturing industry are the main sources of heavy metal ion contamination. Metals such as lead, cadmium, copper, arsenic, nickel, chromium, zinc and mercury have been recognized as hazardous heavy metals.

Heavy metal toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs. Presence of metals in water streams and marine water causes a significant health threat to the aquatic community—most common being the damage of the gill of the fish [1,2]. Consequently, in many countries, more strict legislation has been introduced to control water pollution. Removal of metal ions from wastewater in an effective manner has become an important issue today [3]. Precipitation followed by coagulation has been extensively employed for the removal of heavy metals from water. However, this process usually produces large volumes of sludge consisting small amounts of heavy metals. Membrane filtration is a proven way to remove metal ions but its high cost limits the use in practice [1]. Adsorption is an efficient method for the removal of tracer components from water. Activated carbon-produced by carbonizing organic materials-is the most widely used adsorbent. Activated carbon has shown good metal ion adsorption capacities [4–8]. However, the high cost of the activation process limits the use in wastewater treatment. Over the last few years number of investigations has been conducted to test the low cost adsorbents for heavy metal ion removal. Waste biomass, industrial waste, and mineral waste have been investigated by many workers and biomass has shown better adsorption properties [9].

Plant materials are mainly comprised of cellulose materials that can adsorb heavy metal cations in aqueous medium [10].

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The utilization of agricultural waste materials is increasingly becoming a vital concern because these wastes represent unused resources and in many cases present serious disposal problems. Numerous waste biomass sources are available in different parts of the world, on which some experimental adsorption properties have been reported e.g. rice husk [11–15], peanut shells [16], corn cobs [17], saw dust [18–21] coir dust [22], dry tree leaves and barks [23–27] tea and coffee waste [28–35], rice and wheat bran [36,37] and sea weeds [38–40]. Adsorption of heavy metal ions occurs as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface. Various functional groups are involved such as phosphate, carboxyl, amine and amides. Ion exchange mechanism considers the well-known model of metal binding and proton releasing reaction [2,20,28,30,41–43]. Degree of adsorption and rate of adsorption of metal ions onto waste biomass depend on physical and surface properties of adsorbent, metal ion properties and operating conditions. Therefore, the specific effect of adsorbent properties and operating conditions depends on the *biomass-metal ion* system.

Few researchers have worked on water washed [30,34,31,28] and acid washed [35] tea waste for heavy metal ion removal. However, detailed knowledge of each metal ion–adsorbent system and comparison of the novel adsorbents with commonly used adsorbents are important for decision-making. Most of the previous work on low cost adsorbents is limited to batch experiments using simple agitated beaker tests. Fixed bed columns are widely used in practice but it is noted that the adsorption isotherms obtained by batch experiments do not give accurate scale-up data that can be used for fixed-bed design.

This work investigates the potential of tea waste from Sri Lankan tea in removal of metal ions from aqueous solutions. The optimum operating conditions, equilibrium data and adsorption kinetics for Cu and Pb removal using water washed tea waste were obtained. Fixed bed column tests were conducted to ascertain practical applicability. The adsorption characteristics of tea waste were compared with that of commonly used adsorbent granular activated carbon as a benchmark. Industrial wastewater contains many metal ions and therefore adsorption of Cu and Pb from mixed metal ion solutions was also studied.

2. Materials and methods

2.1. Preparation of the adsorbent

Black tea produced from tea plantations from central highlands of Sri Lanka "high grown tea" was used for the experiments. Soluble and coloured components were removed from tea by washing with boiling water. This was repeated until the water was virtually colourless. The tea leaves were then washed with distilled water and were oven dried for 12 h at 85 °C. The dried tea waste was sieved and stored in sealed polythene bags. The fraction between 350 and 850 μm was used for all the experiments except for the effect of size tests. Coconut shell based Granular Activated Carbon (GAC) provided by Haycarb Ltd., Sri Lanka was used as a benchmark absorbent for com-

parison with tea waste. The GAC was used at the original size, 1298 μm, without any size reduction.

2.2. Synthetic wastewater preparation

Synthetic wastewater solutions were prepared by dissolving analytical grade $Cu(NO_3) \cdot 3H_2O$ and $Pb(NO_3)$ in distilled water to obtain 1000 mg of metal/l solutions. The solution was diluted to the required concentration for experiments. The pH of the solution was measured and observed as 5.5 ± 0.5 and no chemicals were added to change pH.

2.3. Batch adsorption tests

Batch adsorption tests were conducted by mixing known weight of tea waste and 200 ml of solution of known metal ion concentration. Metal ion concentrations used were in the range 25–200 mg/l. The mixture was shaken in a mechanical shaker and 5 ml samples of solution were withdrawn from the bottle at known time intervals. Preliminary experiments showed that adsorption is fast and the removal rate is negligible after 90 min. Therefore, contact time of 90 min were used for batch tests. The sample was filtered to remove any fine particles and analyzed for the metal ion. Series of experiments were conducted to determine the effect of adsorbent dose, initial metal ion concentration and the particle size on adsorption. The solution pH was at 5.5 ± 0.5 and all the experiments were conducted at room temperature $22 \pm 2\,^{\circ}C$.

Tests were conducted to observe effect of competitive metal ion by preparing metal ion solutions containing both Cu and Pb.

2.4. Effect of pH

Effect of initial solution pH on adsorption was determined by mixing 1 g of adsorbent with 100 ml of solution containing metal concentration of 100 mg/l at various pH values ranging from 2 to 7. Solution pH was adjusted with 0.5 M, HCl and NaOH solutions. The mixture was shaken for 1 hr and the solution was filtered and analysed.

2.5. Fixed bed experiments

Fixed bed column adsorption experiments were conducted in a small 3 cm diameter glass column. The column was filled to a height of 10 cm with the known weight of adsorbent. The metal ion solution containing 100 mg/l of Cu or Pb was fed to the column at a constant flow rate of 20 ml/min through the bed using a peristaltic pump. The solution leaving the bottom of the column was collected at various time intervals and the samples were analyzed. Adsorption from mixed metal ion solutions containing 100 mg/l of each metal ion was also tested.

2.6. Isotherm experiments

Equilibrium isotherm experiments were conducted by mixing 1 g of tea waste with 200 ml of solution for a range of initial metal

Table 1
Physical properties of tea waste and granular activated carbon

Property	Tea waste	GAC
Surface weighted mean diameter (μm)	524.22	1234.41
Volume weighted mean diameter (μm)	720.51	1298.49
Surface area (m^2/g)	0.79	683.14
Pore size (nm)	1.92	2.28
Bulk density (kg/m^3)	206.00	469.60
True density (kg/m^3)	1105.50	1754.60

concentrations from 400 to 50 mg/l. The mixture was shaken for 6 h to reach equilibrium and the solution was filtered and analyzed.

The batch and column adsorption experiments were performed in duplicate to observe the reproducibility and the mean value was used for each set of values.

2.7. Metal analysis and adsorbent characterization

Atomic absorption spectrophotometry with an air-acetylene flame and hollow cathode lamps for Cu and Pb was used for metal ion analysis. The absorbance of the samples was read in triplicate. The surface area and particle size of tea waste were measured using BET surface area analyzer (Micromeritics, Tri Star 3000) and back-scattered laser light diffraction (Mastersizer 200, Malvern Instruments), respectively. True and bulk densities of tea waste and GAC were also determined using the specific gravity bottle method.

3. Results and discussion

Physical properties of tea waste and GAC determined as described above are listed in Table 1.

The metal ion concentrations obtained for batch experiments were converted to percentage of metal ion removed and amount of metal adsorbed per unit weight of adsorbent after making necessary corrections for errors due to filtration. The results thus obtained are presented and discussed in this section.

3.1. Effect of adsorbent dose

Effect of adsorbent dose on percentage removal of Pb and Cu ions is shown in Figs. 1 and 2. Percentage of lead ion removal increased from 37 to 94% when the adsorbent dose per 200 ml of solution was increased from 0.25 to 1.5 g. A similar trend was shown by Cu adsorption. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal removal at a high dose. However, as shown in Fig. 3 the amount of metal ions adsorbed per unit weight of adsorbent (q) decreases with the adsorbent dose. This is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of 'q' indicating the adsorption sites remain unsaturated.
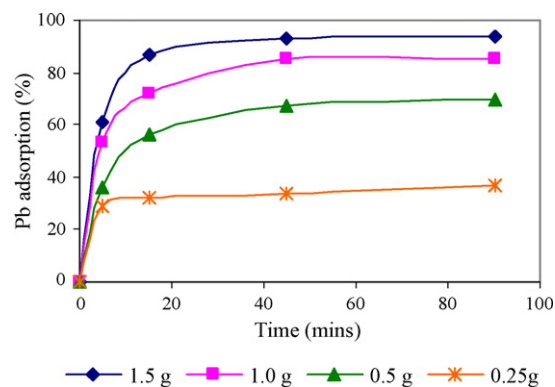

Fig. 1. Effect of adsorbent dose on adsorption of Pb onto tea waste: 200 ml of 200 mg/l metal solution, 22 °C.
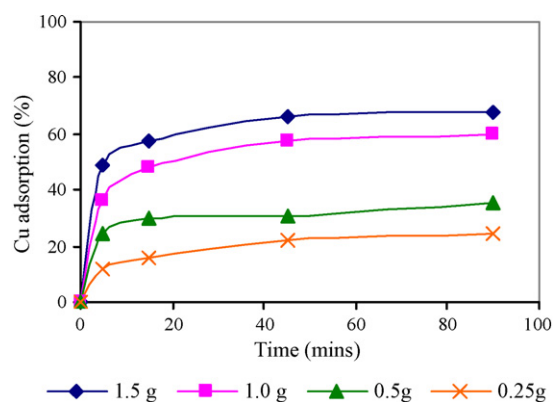

Fig. 2. Effect of adsorbent dose on adsorption of Cu onto tea waste: 200 ml of 100 mg/l metal solution, 22 °C.

3.2. Effect of initial metal ion concentration

Figs. 4 and 5 show percentage of ion removal as a function of time for a range of Pb and Cu ion concentrations. Ion removal percentage increases when the initial ion concentration decreases. At low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, amount of metal adsorbed per unit weight of adsorbent, q, is higher at high concentrations as shown in Fig. 6.
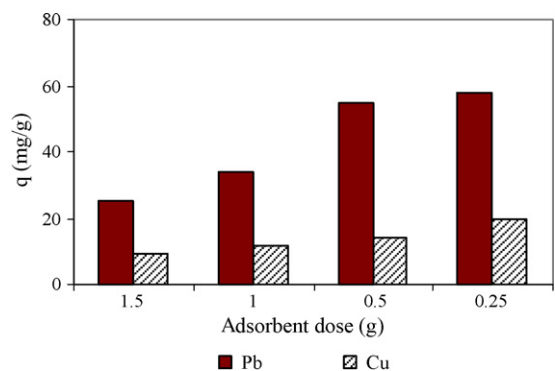

Fig. 3. Comparison of adsorption capacities of Cu and Pb onto tea waste: 200 ml of solution at 22 °C.
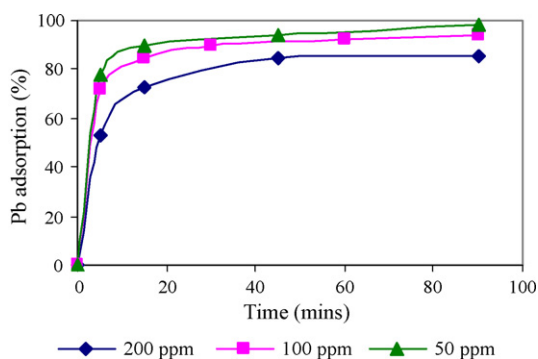
Fig. 4. Effect of initial solution concentration on adsorption of Pb onto tea waste: 1 g of tea mixed with 200 ml of solution, 22 °C.
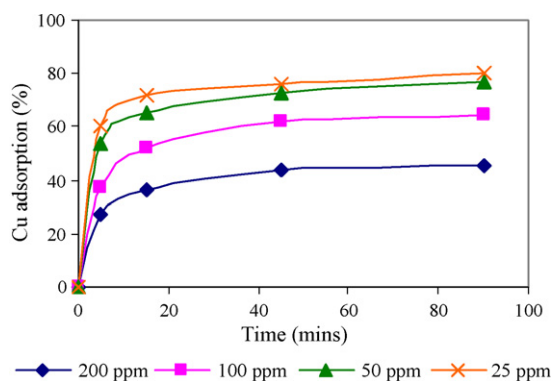

Fig. 5. Effect of initial solution concentration on adsorption of Cu onto tea waste: 1 g of tea mixed with 200 ml of solution, 22 °C.

3.3. Adsorption isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships [44]. Langmuir model originally developed for adsorption of gases onto solids is based on the assumption that adsorption occurs on localized sites with no interaction between adsorbate molecules and maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. For solid–liquid systems the linear form of the
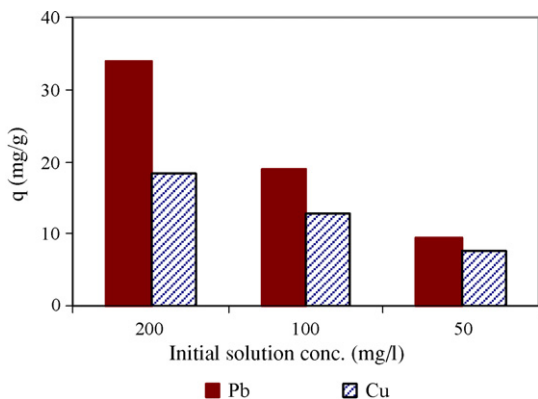

Fig. 6. Comparison of adsorption capacities of Cu and Pb onto tea waste: 1 g of tea mixed with 200 ml of solution at 22 °C.
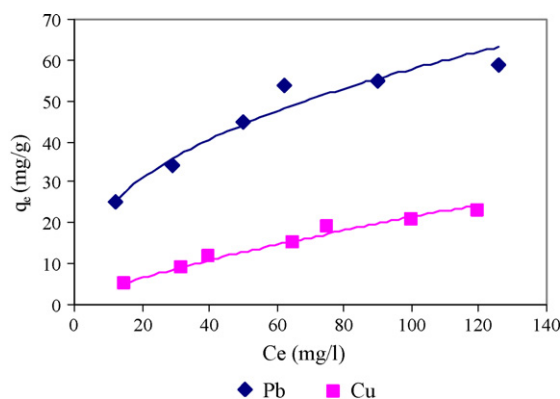

Fig. 7. Adsorption isotherms for Cu and Pb onto tea waste at 22 °C (Eq. (2)).

Table 2
Langmuir and Freundlich isotherm constants for Pb and Cu onto tea waste at 22 °C

Metal	Freundlich constants			Langmuir constants		
	k	$1/n$	R^2	q_0	b	R^2
Cu	0.7012	0.7427	0.9845	48	0.0076	0.9947
Pb	9.6532	0.3885	0.9614	65	0.0494	0.9579

isotherm can be expressed by the Eq. (1):

$$\frac{1}{q_e} = \frac{1}{bq_0C_e} + \frac{1}{q_0} \tag{1}$$

Freundlich isotherm model is the empirical model for adsorption and expressed as

$$q_e = kC_e^{1/n} \tag{2}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium, q_0 the amount of solute adsorbed per unit weight of adsorbent corresponding to complete coverage of available sites, C_e the residual liquid phase concentration at equilibrium, b the adsorption coefficient, and k and n are the constants related to adsorption capacity and adsorption intensity.

Adsorption isotherms for Cu and Pb (q_e versus C_e) are shown in Fig. 7. The experimental data were fitted to both Langmuir and Freundlich isotherms and the isotherm constants in Eqs. (1) and (2) and the regression coefficients (R^2) are given in Table 2. $1/n$ values for both Cu and Pb lie between 0 and 1 indicating favorable adsorption. Pb shows higher adsorption capacity and affinity compared to Cu.

The results discussed so far indicate a higher adsorption of Pb compared to Cu for the experimental conditions under observation. This may be explained by the hydration enthalpy which is the energy that permits the detachment of H_2O molecules from cations and then reflects the easiness for the ion to interact with the functional groups on tea waste particles. The more a cation is hydrated the stronger its hydration enthalpy and then less it could interact with the adsorbent [7,25]. Hydration enthalpies[1] of Pb

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[1] Values obtained from: http://www.science.uwaterloo.ca/~cchieh/cact/applychem/hydration.html.

Table 3a

Langmuir constants (q_0) for adsorption of Cu onto various types of waste biomass reported in literature

Adsorbent	Treatment given	q_0 (mg/g)	Reference
Saw dust	None	2	[20]
	None	3	[18,19]
	NaOH modifeid	7	
Sunflower stalks	None	29	[10]
Tea waste	Acid washed	27	[35]
	None	9	[30]
	None	48	This work
Rice husk	None	29	[12]
	Tartaric acid modified	29	[14]
Cassava waste biomass	None	71	[45]
	Acid treated	85	
Tree leaves (elaeagnifolium)	None	13	[24]
	NaOH modified	20	
Tree barks (coniferous)	None	7	[25]
	Formaldhyde treated	48	[26]
Melon seed husks	None	8	[46]
	EDTA modified	16	
Wheat bran	None	15	[36]
Sago waste	None	12	[47]
Coffee residue	Bind with clay	31	[29]

and Cu are −1481 and −2100 kJ/kg, respectively. This indicates theoretically high affinity of Pb cations to the adsorbent and hence higher removal of Pb compared to Cu.

Many workers have experimented other waste biomass as low cost adsorbents for metal ion removal. Langmuir constants, q_0, values obtained for adsorption of Cu and Pb onto various other biomass types reported in the literature are listed in Tables 3a and 3b. However it should be noted that adsorp-

Table 3b

Langmuir constants for adsorption of Pb onto various types of waste biomass (q_0) reported in literature

| Adsorbent	Treatment given	q_0 (mg/g)	Reference
Saw dust	None	3	[20]
Tea waste	Acid washed	79	[35]
	None	2	[28]
	None	65	This work
Rice husk	None	11	[12]
	Tartaric acid modified	108	[14]
Peach stone	None	0.0023	[48]
Apricot stone	None	0.0013	
Cocoa shells	None	33	[43]
Tree leaves	None	21	[24]
	NaOH modified	47	
Tree barks	None	21	[25]
	Formaldhyde treated	108	[26]
Wheat bran	None	64	[36]
Sago waste	None	47	[47]
Coffee residue	Bind with clay	20	[29]
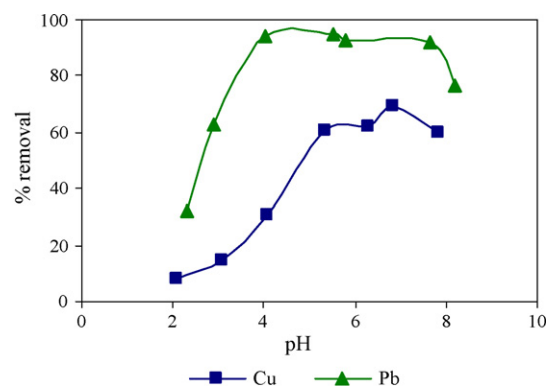
Fig. 8. Effect of pH on adsorption of Cu and Pb onto tea waste: 1 g of mixed with 100 ml of 100 ppm solution at 22 °C.

tion characteristics largely depend on many parameters such as particle size, pH of the solution and the results presented on Tables 3a and 3b are based on experiments conducted under different operating conditions. Higher values of q_0 are reported for Pb compared to Cu. This agrees with the results of the present work. Results show that tea waste is a better adsorbent compared to some of the biomass used. Treated biomass shows higher adsorption capacities compared to untreated material. However, treatments increase the cost and may add other chemicals to the water streams and should be taken into account.

3.4. Effect of solution pH

Fig. 8 shows percentage of metal ion adsorbed on to tea waste as a function pH. Cu and Pb adsorption show maximum removal in the pH range 5–7. At pH 2–3 range the adsorption is very low and rapidly increases between pH 4 and 5. This phenomenon can be explained by the surface charge of the adsorbent and the H⁺ ions present in the solution. At low pH the cations compete with the H⁺ ions in the solution for the active sites and therefore lower adsorption. The surface charge of the biomass materials is a strong function of the pH. Zeta potential of tea waste particles at pH 3, 4, 5 and 6 are −14, −24, −23 and −22 mV respectively [34]. Therefore at high pH values surface of the adsorbent has a higher negative charge which results higher attraction of cations. These data are in agreement with the results obtained for other biomass materials such as coffee residues [29], orange waste [42], coca shells [43], sago waste [47] and saw dust [18,21] by many workers. At very high pH values the metal complex forms and results precipitation and therefore the separation may not be due to adsorption [4,18,49]. Hence adsorption of Cu and Pb cations onto tea waste is at optimum in the pH range 5–6.

3.5. Effect of particle size

Surface area of the adsorbent is an important parameter for adsorption. Exposure of adsorbent sites for solid-metal ion interaction is high if the surface area of adsorbent is high. The smaller the particle size the higher the surface area per unit weight of adsorbent and hence higher percentage of metal removal is expected. The results showed that for tea waste particles of mean

size 1250, 925 and 575 µm the percentage of Cu ion removal were 41, 53 and 57, respectively. Other low cost adsorbents such as rice husk, saw dust have shown similar effects of particle size on adsorption [12,19].

3.6. Adsorption kinetics

Adsorption kinetics describes the solute uptake rate which intern controls the residence time and hence the size of the adsorption equipment. The experimental results for tea waste show rapid initial adsorption rate followed by a slower rate. Initially, the adsorption sites are open and the metal ions interacts easily with the site and hence a higher rate of adsorption is observed. Further, the driving force for adsorption – the concentration difference between the bulk solution and the solid-liquid interface – is higher initially and this results a higher adsorption rate. However, after the initial period slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent. Several adsorption kinetic models have been developed to understand the adsorption kinetics and rate limiting step [6,8,50–53].

The following models have been widely used [50] Lagergren pseudo first order model can be expressed by Eqs. (3) and (4):

$$\frac{dq}{dt} = k_1(q_e - q) \tag{3}$$

$$\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303} \tag{4}$$

The pseudo-second order model are given by Eqs. (5) and (6):

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{5}$$

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{6}$$

where q and q_e are the amount of metal adsorbed per unit weight of adsorbent (mg/g) at time t, and at equilibrium, respectively, and k_1 and k_2 are the adsorption rate constants. The initial adsorption rate (h) is equal to $k_1 q_e$ and $k_2 q_e^2$ (mg g^{-1} min^{-1}) for first and second order models, respectively.
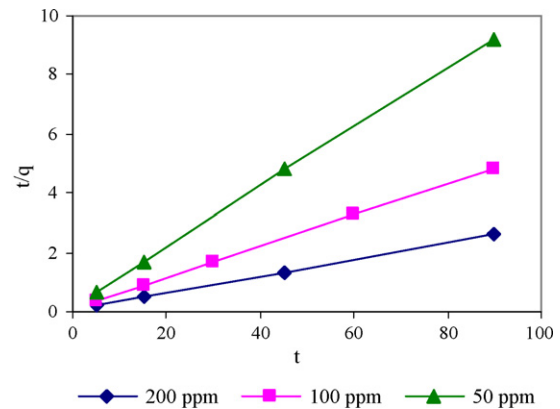

Fig. 9. Pseudo-second order kinetics of Pb on tea: 1 g of tea waste mixed with 200 ml of solution, 22 °C.
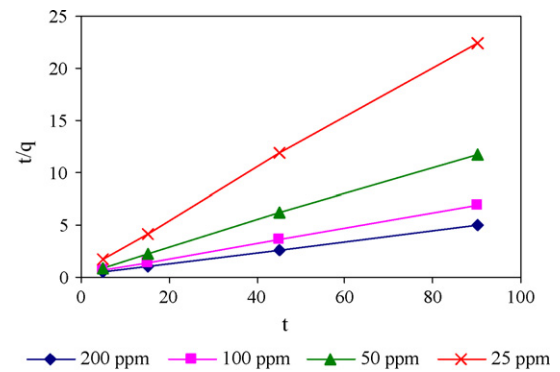

Fig. 10. Pseudo-second order kinetics of Cu onto tea: 1 g of tea waste mixed with 200 ml solution, 22 °C.

The results obtained for adsorption of Cu and Pb onto tea waste was fitted to Eqs. (4) and (6). Pseudo-second order model provides better correlation than pseudo first order model. The plots of t/q versus t for the linear second order model are shown in Figs. 9 and 10. The kinetic parameters calculated are shown in Table 4. The equilibrium sorption capacities determined using second order model were in agreement with the experimentally determined equilibrium sorption capacities. The initial adsorption rate (h) increases with the initial solution concentration for both Cu and Pb. The rate constant decreases with the solution

Table 4
Second order kinetic parameters for adsorption of Pb and Cu onto tea waste

Metal	Initial solution concentration (mg/l)	Initial adsorption rate, h (mg g^{-1} min^{-1})	Rate constant, k_2 (g mg^{-1} min^{-1})	Amount adsorbed experimental, q_{exp} (mg/g)	Amount adsorbed predicted, q_{pre} (mg/g)	R^2
Cu	200	5	0.0133	18	19	0.9999
	100	3	0.0170	13	14	1
	50	3	0.0427	8	8	0.9997
	25	2	0.1268	4	4	0.9996
Pb	200	11	0.0091	34	35	0.9997
	100	10	0.0283	19	19	0.9999
	50	6	0.0586	10	10	0.9998
Cu						
1250 µm	100	2	0.0269	8	9	0.9958
925 µm	100	3	0.0205	11	11	0.999
575 µm	100	4	0.0280	12	12	0.9997

Table 5
Comparison of Cu and Pb adsorption onto tea waste and GAC

Metal	Adsorbent dose (g)	Initial solution concentration (mg/l)	% Removed	Amount adsorbed (mg/g)	Initial adsorption rate, h (mg g^{-1} min^{-1})	Second order rate constant, k_2 (g mg^{-1} min^{-1})
Pb	1.5	200	94 (95)	25 (25)	12 (4)	0.0173 (0.0058)
	1.0	200	85 (73)	34 (29)	11 (6)	0.0091 (0.0064)
	0.5	200	70 (46)	56 (37)	12 (6)	0.0035 (0.00034)
	0.25	200	37 (30)	59 (48)	22 (9)	0.0061 (0.0036)
	1.0	100	94 (72)	19 (15)	10 (4)	0.0283 (0.0172)
Cu	1.0	200	46 (36)	18 (14)	5 (1)	0.0133 (0.0020)
	1.0	100	65 (66)	13 (13)	3 (1)	0.0171 (0.0056)
	1.0	50	77 (84)	8 (8)	3 (1)	0.0427 (0.0167)

Values within parentheses are for GAC under the same conditions as for tea.

concentration. At high concentration the difference between the metal ion concentration in the solution and that on the solid-liquid interface, which is the driving force for the adsorption is high and therefore higher initial adsorption rates are shown at higher solution concentrations. Pb shows higher adsorption rate compared to Cu for all concentrations. The results also show that the initial adsorption rate is high for smaller particles despite there being no significant difference in rate constants.

3.7. Comparison of tea waste with GAC

Activated carbon is the commonly used adsorbent in practice. Experiments were conducted to compare the adsorption characteristics of tea waste with granular activated carbon. The results are presented in Table 5. The tea waste matter shows higher percentage removal for most of the experiments compared to GAC. Initial rate of adsorption and rate constants for GAC are always lower than that for tea waste. GAC has a higher surface area compared to tea waste. However, the diffusion of metal ions to the interior of the GAC may not occur and hence shows lower adsorption. This may be partly due to the higher particle size and sphericity of GAC compared to tea waste. Metal cations may also have higher affinity to the surface of tea waste compared to GAC. However, adsorption capacity and rate for Pb onto GAC was higher than that for Cu. This is a similar trend as that for tea waste. GAC shows better adsorption than tea waste for some experiments. It can be concluded that tea waste is better or at least equally good as GAC for removal of Cu and Pb from aqueous solutions.

3.8. Effect of mixed ions

Industrial wastewater normally contains many metal ions as a mixture. Tests were performed to investigate the influence of Pb on the uptake of Cu and vice versa. Figs. 11 and 12 present results obtained for the removal of metal ions from mixed solutions. Results obtained for removal of ions from single ion solutions are also presented for comparison. Percentage removal and mass of metal adsorbed from mixed solutions are listed in Table 6. Significance reduction in the Pb removal was observed in the presence of Cu. Reduction in Pb adsorption in the presence of Cu was 41% and 18% for solution concentrations of 200 and 100 mg/l respectively. However, Cu adsorption was reduced only
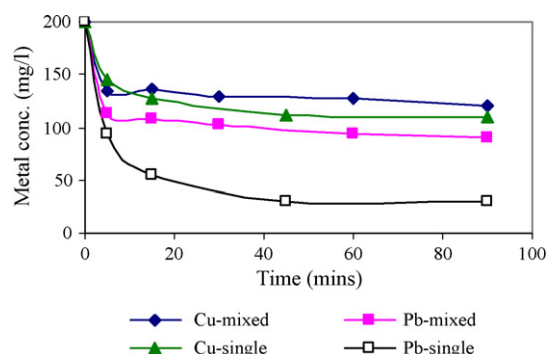

Fig. 11. Comparison of adsorption from mixed and single ion solutions onto tea waste at 22 °C.

by 12 and 13% for 200 and 100 mg/l solutions. Total amount of metal adsorbed per unit weight of adsorbent increased in all concentrations of mixed solutions compared to that at single metal ions. This indicates that different adsorption mechanisms may be involved in adsorbing Cu and Pb ions.

3.9. Fixed bed adsorption

Batch adsorption tests provide information on adsorption equilibrium characteristics and adsorption kinetics. However, batch operations are not economical in practice and data on fixed bed column operations are essential for industrial adsorber design. Column experiments were conducted to understand the adsorption behavior in fixed bed columns and to determine
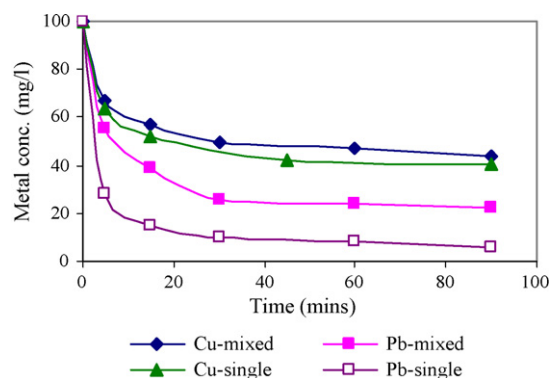

Fig. 12. Comparison of adsorption from mixed and single ion solutions onto tea waste at 22 °C.

Table 6
Results on adsorption of Cu and Pb from mixed solutions

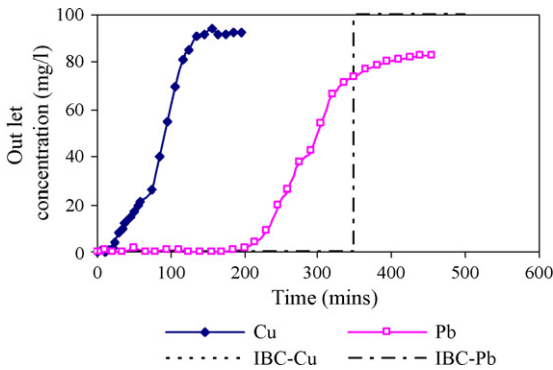| Initial solution concentration (mg/l)		% Adsorbed		Amount adsorbed (mg/g)	
Cu	Pb	Cu	Pb	Cu	Pb
200	200	40	55	16	20
100	100	56	77	11	15
50	50	73	92	7	9

Fig. 13. Breakthrough curves for adsorption of Cu and Pb onto tea waste: 15 g of tea, flow rate-20.

deviation from batch operations. Results on fixed bed column experiments are presented and discussed in this section.

Breakthrough curves for Cu and Pb adsorption onto tea waste and GAC from single metal ion solutions of concentration 100 mg/l are shown in Figs. 13 and 14. Breakthrough curves for Cu and Pb adsorption from mixed solution containing 100 mg/l of each metal onto tea waste is shown in Fig. 15. Typical 'S' shaped curves were obtained for all experiments. However, results show that when the concentration of the solution leaving the column reaches 85–95 mg/l the concentration changes very slowly and hence the full bed exhaustion is achieved at almost infinite time.

The area above the breakthrough curve is a measure of the bed capacity (BC) and is given by [54]:

$$BC = G \int_0^T (C_0 - C)\, dt \qquad (7)$$

where G is the solution rate in l/min, C_0 and C are the inlet metal ion concentration and outlet metal ion concentration in
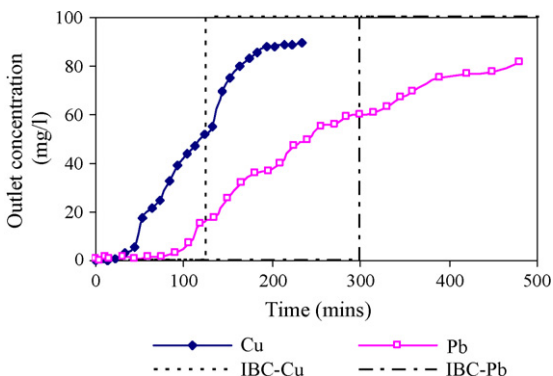

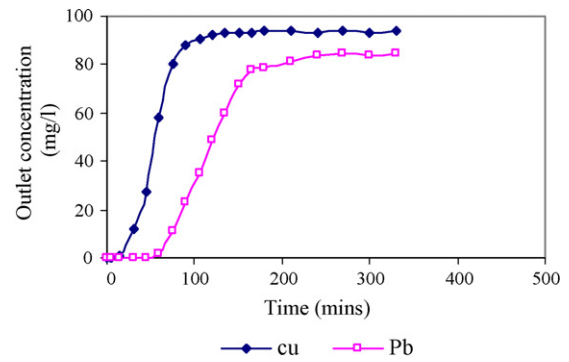Fig. 14. Breakthrough curves for adsorption of Cu and Pb onto GAC: 32 g of GAC, flow rate-20 ml/min.

mg/l at time t, respectively, and T is the actual time required for full bed exhaustion. If the adsorption is infinitely rapid an ideal breakthrough curve will be a step change. Ideal breakthrough curves were estimated for all the experimentally determined curves and time required for full bed exhaustion under ideal condition (T_s) was calculated. Ideal breakthrough curves (IBC) thus obtained are shown by dotted lines in Figs. 13 and 14. In industry, fixed bed adsorber operation is stopped when the outlet concentration reaches the maximum allowable condition (breakthrough concentration). At this breakpoint the bed is not fully utilized and the equivalent length of the unused bed, LUB, is given by [54]:

$$LUB = \frac{Z}{T_s}(T_s - T_b) \qquad (8)$$

The bed capacity (BC) is then given by

$$BC = G(C_0 - C^*)T_s \qquad (9)$$

where Z is the bed height, C^* the concentration of the solution in equilibrium with the fresh adsorbent or concentration of the solution leaving the bed initially, T_s the time required for full bed exhaustion at infinite rapid adsorption and T_b is the breakthrough time.

The BC, LUB, T_s, T_b values thus obtained for experimentally determined breakthrough curves are summarized in Table 7. C^* is 0 for both tea waste and GAC indicating that fresh adsorbent is in equilibrium with solution of zero metal ion concentration. A bed height of 10 cm was maintained for both GAC and tea waste to maintain same residence time for solution in the column. Therefore, when comparing results for GAC and tea waste in Table 7 the difference in bed weight should be taken into account. Higher metal ion adsorption and lower LUB was observed for Pb compared to Cu for both tea and GAC. This indicates a higher

Fig. 15. Breakthrough curves for adsorption from mixed solutions onto tea waste: 15 g, 20 ml/min.

Table 7
Results on adsorption of Cu and Pb in fixed bed column 10 cm height, 3 cm diameter, 20 ml/min flow rate, 100 mg/l solution concentration

Adsorbent (weight in g)	Metal	T_s (min)	T_b at $C/C_0 = 0.2$ (min)	LUB (cm)	Amount adsorbed at T_b		Amount adsorbed at full bed exhaustion	
					Total (mg)	mg/g	Total (mg)	mg/g
Tea (15)	Pb	350	250	2.85	490	33	700	46
Tea (15)	Cu	95	55	4.63	90	6	190	13
GAC(32)	Pb	300	140	5.33	260	8	600	19
GAC(32)	Cu	125	55	5.60	95	3	250	8

Table 8
Maximum adsorption capacities of various metals onto tea waste reported in literature

Reference	Maximum adsorption capacity, q_0 (mg/g)						
	Cu	Pb	Cd	Ni	Zn	Cr^{6+}	Fe
[35][a]	27	79	31		12		
[30]	9		11				
[34]				15			
[31]						455	
[28]		9		5	11		24
This work	48	65					

[a] Acid washed tea waste.

capacity and higher adsorption rate for Pb. Comparing tea with GAC, tea waste shows higher adsorption capacity and lower LUB values indicating higher adsorption rate. These results on column tests show a similar trend as batch experiments. However, compared to batch experiments adsorption capacities in column were approximately 40 and 20% lower for Cu and Pb, respectively, which can be due to following reasons. In batch experiments the mixture was shaken continuously and good interaction between the solid and solute was achieved. In the fixed bed, adsorbent is packed in the column and surface of the solid particles are in contact with each other and therefore results a less solid-solute interaction. Further, liquid channeling which results poor solid-metal ion contact and less residence time may occur in the column. Therefore bed adsorption capacities are lower compared to batch operation.

Above results shows that tea waste can be used as low cost adsorbent for removal of Cu and Pb from wastewater. Tea waste has shown good adsorption capacities for other metal ions such as Ni, Cd, Cr and Zn. Table 8 lists adsorption capacities of various metal ions onto tea waste reported by previous workers. The exact adsorption capacities will depend on the operating conditions and the source of tea waste. However, the results in Table 8 show tea waste has a good adsorption capacity for all the metal types commonly present in wastewater.

4. Conclusion

Tea waste is a good adsorbent for removal of Cu and Pb from wastewater. Pb showed higher adsorption capacity and rate compared to Cu. The adsorption rate was rapid over a initial period of time and then decreases gradually. The adsorption kinetics fit to pseudo second order model, which is based on the assumption chemisorption is the rate limiting step. Removal of metal

ions was at highest around solution pH 5–6. Adsorption rate and adsorption capacity depended on the adsorbent dose, solution concentration and particle size. The fixed bed column results showed similar trend as batch experiments. However, adsorption capacities were lower compared to batch experiments.

Comparison of tea waste with GAC shows tea waste is better or at least equally good as GAC in batch operation. Adsorption was always rapid for tea waste compared to GAC. Adsorption capacities of GAC in the fixed bed column were much lower than for tea waste. This may be due to different channeling effects of tea waste and GAC. The difference in adsorption rates onto tea waste and GAC may also contributed to the adsorption capacity difference in the column.

Adsorptive properties of waste biomass largely depend on the source of biomass and treatments given to the adsorbent. The physical and chemical properties of the adsorbent such as surface area, surface functional groups, surface charge and particle size determines the adsorption characteristics of a material. The surface properties of the waste biomass can be improved by various thermal and chemical treatments given to the adsorbent prior to adsorption [13,14,16–18,22,24,26,27,46,55]. However, this may incur cost and also lead to addition of other chemicals to the water. Metal ion properties such as mobility of the ion, ionic radius, hydration enthalpy control the adsorption of a particular ion onto adsorbent. Solution pH, contact time and the mode of adsorbent–adsorbate contact are the main operating conditions which affects the adsorption capacity and the rate.

Tea waste used for this work was not treated chemically or thermally. However, results show that tea waste is a better adsorbent compared to some of the treated biomass materials. Therefore, tea waste obtained from Sri Lankan tea waste can be used as a low cost adsorbent for the removal of heavy metal ions from industrial wastewater. Tea waste is available in the tea factories and cafetarias. However a suitable mechanism for collection and storing of tea waste should be taken into account. Further investigations are needed for desorption studies, economically feasible regeneration of the adsorbent and application of the adsorbent for real industrial wastewater. However, in many parts of the world where tea waste is available at low or no cost, regeneration is not required and the metal laden biomass can be disposed by incineration [2].

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