

Removal of Pb(II) from aqueous solution by adsorption using activated tea waste

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(Received 17 January 2009 • accepted 11 June 2009)

Abstract—A basic investigation on the removal of Pb(II) ions from aqueous solutions by using activated tea waste was conducted in batch conditions. An inexpensive and effective adsorbent was developed from waste tea leaves for the uptake of Pb(II) from aqueous solution. The influence of different experimental parameters—shaking time, particle size, adsorbent dose, initial pH, temperature, etc.—on lead uptake was evaluated. Lead is adsorbed by the developed adsorbent up to maximum of 99.7%. The initial Pb(II) concentrations were 5, 10, 15 and 20 mg/l in the experiment. The adsorption was found to be exothermic in nature. The Langmuir, Freundlich and Tempkin isotherm models were tried to represent the equilibrium data of Pb(II) adsorption. The adsorption data was fitted very well to the Langmuir isotherm model in the studied concentration range of Pb(II) adsorption. Isotherms have been used to determine thermodynamic parameters of the process: free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). Column experiments were performed to study the practical applicability of the system. The kinetics and the factors controlling the adsorption process were also discussed. Activated tea waste is a better adsorbent compared to other adsorbents available in literature.

Key words: Adsorption, Pb(II), Kinetics, Adsorption Isotherms, Activated Tea Waste

INTRODUCTION

Heavy metals are major pollutants in marine, ground, industrial and even treated waste waters. Stringent regulations are increasing the demand for new technologies for metal removal from waste water to obtain today's toxicity driven limits [1]. The major sources of lead release into the environment by waste streams are battery, paper and pulp, mining, electroplating, lead smelting and metallurgical finishing industries. The adverse health effects due to lead are well documented, and it has been reported to cause visual disturbances, convulsions, constipation, anemia, vomiting, nausea, severe abdominal pain and gradual paralysis in the muscles. Lead also affects the central nervous system, peripheral nervous system, and hematopoietic, renal, gastrointestinal, cardiovascular, and reproductive system [2]. Therefore, the removal of Pb(II) ions from water prior to supplying water for drinking, bathing etc., is very important and urgent.

A number of methods are available for the removal of Pb(II) from aqueous solutions: ion exchange, solvent extraction, membrane process, chemical precipitation and adsorption. Adsorption has many advantages over other methods including recovery of metal value, selectivity, sludge-free operation, cost effectiveness and meeting of strict discharge specification.

A number of adsorbents such as bagasse fly ash [2], red mud [3], coconut shell carbon [4], activated phosphate [5], olive cake [6], bentonite clay [7], activated carbon [8], saw dust [9], etc., have been used for Pb(II) removal. Among these materials, the use of some natural materials [10] for the removal of Pb(II) has been very successful. In recent years, low cost adsorbent developed from such

type of materials [11-14] has gained attention due to its double benefit of resource generation and pollution abatement. Few researchers have experimented on water-washed [15,16] and acid-washed tea waste [17] for Pb(II) removal. However, alkali-washed tea waste for Pb(II) removal has not yet been attempted by any researcher. In the present work, an attempt has been made to develop an inexpensive adsorbent system for the removal of Pb(II) from aqueous solution using waste tea leaves. Most of the adsorption experiments were conducted in batch mode. Column studies were also tested to ascertain practical applicability. Several factors affecting the removal process have been studied. Applicability of adsorption isotherms on the removal process has been tested and the kinetics as well as factors controlling the adsorption have also been determined.

EXPERIMENTAL

All chemicals and reagents used were of the analytical reagent grade and obtained from E. Merck, India. The pH of the solution was measured by using pH meter (LI 120, Elico India). A shaking incubator (Model NSW-256, Calton, New Delhi, India) was used for shaking to carry out the batch adsorption experiments. An oven (S. M. Scientific Instruments Pvt. Ltd., New Delhi, India) was used for drying the adsorbent. The particle size of adsorbent was determined by sieve analysis. The cation exchange capacity was determined by Na saturation method [10]. The concentration of Na in the solution was determined using a Perkin Elmer 3110 atomic absorption spectrophotometer. The acidic groups present in the adsorbents were calculated by the method proposed by Boehm and Voll [18]. The surface area of the adsorbent was measured by a surface area analyzer (Quantasorb model, QS-7). The porosity and density of the adsorbent were determined by mercury porosimeter and specific gravity bottles, respectively.

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1. Adsorbent Development

Waste tea leaves produced from domestic tea making process were used for adsorbent development. These leaves were washed thoroughly with boiling water to remove traces of tea. The washed tea waste was then dried in sun light for 8 h to remove moisture and ground. The idea for enriching the sulfur content of the adsorbent is that Pb(II) has more affinity of sulfides than other anions as can also be seen from natural occurrence of the most of the metals in their sulfide form [19]. To enrich the sulfur percentage 99.5 g of tea waste was immersed for 24 h in minimum amount of distilled water containing 0.5 g of Na_2S . Then the mixture was filtered to separate filtrate, and filtered solid was air dried under ambient conditions. The dried sample was washed with distilled water for several times till it gave nil concentration of sulfide and was oven dried for 4 h at 110 °C. The dried sample was sieved to the desired particle size before use. The material was stored in a vacuum desiccator for further use.

2. Adsorbent Characterization

The rate of removal of pollutants from waste water by an adsorbent is significantly affected by the physico-chemical nature of the adsorbent. Therefore, any adsorbent should be characterized for determining its relevant physical properties and chemical composition. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer.

2-1. X-ray Diffraction Analysis

X-ray diffraction of adsorbent (activated tea waste) after adsorption was obtained by a Phillips X-ray diffractometer employing nickel filtered CuK_{α} radiation.

2-2. Determination of Point of Zero Charge

The pH of the solution affects the surface charge of the adsorbents as well as the degree of the ionization and speciation of different pollutants. Change in the pH affects the adsorptive process through dissociation of functional groups as the active sites on the surface of the adsorbent. This subsequently leads to a shift in the reaction kinetics and the equilibrium characteristics of the adsorption process. Adsorption of the various anionic and cationic species on such adsorbents can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbate. It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to deposition of OH^- ions. The point of zero charge of the adsorbent was determined by the solid addition method. A 50 ml of 0.1 M KNO_3 solution transferred into a series of 100 ml conical flask. The initial pH (pH_i) values of the solution was adjusted from 1.0 to 10.0 by adding either fixed strength of HNO_3 (0.05, 0.1 and 0.5 N) or 0.1 N KOH . Then 1.5 g of activated tea waste was added to each flask which was securely capped immediately. The flasks were then placed into a constant temperature water bath shaker and shaken for 24 h. The pH values of the supernatant liquid were noted after 24 h.

3. Lead Solutions

Stock lead solution (100 mg/l) was prepared by dissolving 0.160 g $\text{Pb}(\text{NO}_3)_2$ in deionized distilled water with addition of 2-3 drops of concentrated HNO_3 . The stock solution was diluted with distilled water to obtain desired concentration ranging from 0.5 to 20 mg/l.

4. Determination of the Lead Contents in the Solutions

The concentration of lead in the solutions was determined by a

tomic adsorption spectrophotometer (Perkin Elmer Model 3110) using air acetylene flame. The lead standards prepared were checked with standard reference material obtained from the National Bureau of Standards, USA before each lead analysis and the deviation found was insignificant. Average values of five replicates were taken for each determination. Quantification of lead was based upon calibration curves of standard solutions of lead. The detection limit of lead was 0.0001 mg/l. The precision of the analytical procedure, expressed as the relative standard deviation, ranged from 5% to 8%. The precision for the analysis of standard solution was better than 5%.

5. Batch Adsorption Studies

Batch adsorption experiments were carried out for the selection of efficient adsorbent to remove Pb(II) from the solution. A suitable adsorbent was selected by comparing the shaking time and the economical factor such as the cost of adsorbent. Activated carbon, silica gel and activated tea waste were considered for the comparison study. The comparison was carried out by taking a fixed amount of adsorbent (1.0 g for 5 mg/l and 1.5 g for 20 mg/l Pb(II) concentration) in 100 ml aqueous lead solution in a 250 ml glass stopped conical flask. The conical flasks were then placed in a shaking incubator. The temperature and the shaking speed were adjusted at 293 K and 160 rpm, respectively. The conical flasks were taken out from the shaker at a regular time interval of 15 min. The contents of the flask were filtered using Whatman (no. 1) filter paper and the filtrate was analyzed for final pH and final Pb(II) concentrations. Percent Pb(II) removal was calculated as:

$$\text{Percent Pb(II) removal} = [(C_i - C_f)/C_i] * 100 \quad (1)$$

The amount of adsorption at equilibrium (Q_e) was calculated as follows:

$$Q_e = [(C_i - C_f)/m] * V \quad (2)$$

Where C_i and C_f are the initial and final Pb(II) concentration, respectively. C_e is the concentration of Pb(II) in solution at equilibrium. V is the volume of the solution and m is the mass of adsorbent used.

The effects of shaking time (0-90 min), average particle size (85-510 μm), adsorbent dose (0.5-2.5 g in 100 ml), initial concentration (5-20 mg/l), initial pH (1.0-7.0), and temperature (283-323 K) were studied. The initial pH of the adsorbate solution was adjusted using concentrated HNO_3 and NaOH . Adsorption isotherm experiments were also performed by agitating 1.5 g of adsorbent with 100 ml of the varying concentrations of Pb(II) (5-20 mg/l) at different temperatures (283-323 K). The initial pH of the suspension was adjusted to 5.8. After the shaking time (45 min) was established, the suspensions were withdrawn and the amount of Pb(II) in the solution was estimated. All the experiments were performed in duplicate and the mean values are presented.

6. Column Studies

Column for this study was made of borosilicate glass of 10 mm diameter. The sampling point after the column was provided for drawing the effluent samples at regular time intervals. Previously activated tea waste is packed up to a desired bed height (0.3, 0.4 and 0.5 m) in the column. Columns are mounted vertically and glass wool used at the bottom of the column acts as supporting material of the adsorbent bed and also serves the purpose of filtration of the adsorbent particles. Control valves after the over head tank to regu-

late the flow and a graduated burette to measure the influent liquid flow rate (3.0, 6.0, 10.0 and 12.0 ml/min) are incorporated in the feed line of the column. After maintaining the particular flow rate, the feed containing a fixed initial concentration of Pb(II) (2.0, 5.0, 8.0 and 10.0 mg/l) is introduced in the operating column. The effluent samples were collected at a regular time interval of 1.5 h. All the experiments were at room temperature 303 ± 2 °K and initial pH of 5.8.

RESULTS AND DISCUSSION

1. Comparison Study for Selecting Suitable Adsorbent

Three different adsorbents, namely silica gel, activated carbon, activated tea waste, were taken for the comparison study. The percent Pb(II) removal efficiencies of these adsorbents are plotted against time for known amount of adsorbent doses of 1.0 and 1.5 g corresponding to the initial concentrations of 5 and 20 mg/l Pb(II) solution, respectively, in Figs. 1 and 2. It can be observed that silica gel gives maximum removal efficiencies of about 55.3 and 50.6% at concentrations of 5 and 20 mg/l for 30 min. Activated carbon shows maximum removal efficiencies of 99.2% for 5 mg/l of Pb(II) concentration and 91.5% for 20 mg/l Pb(II) concentration at about 50 min. Activated tea waste shows maximum removal efficiencies of 99.7% and 92.5% for Pb(II) concentrations of 5 and 20 mg/l, respectively, at 45 min. So activated tea waste has been chosen for the adsorption study as an efficient adsorbent because it shows maximum removal efficiencies in both of the Pb(II) concentrations and

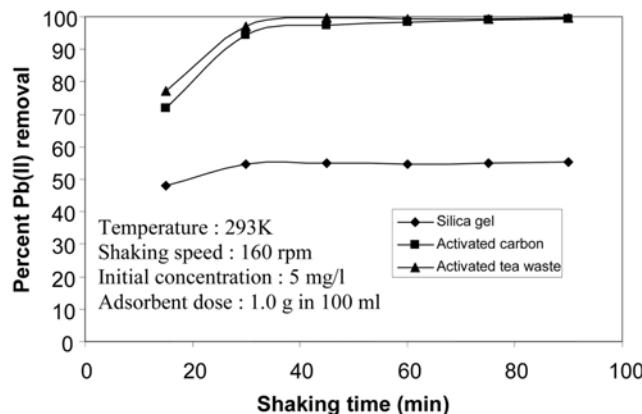


Fig. 1. Comparison study for selecting suitable adsorbent.

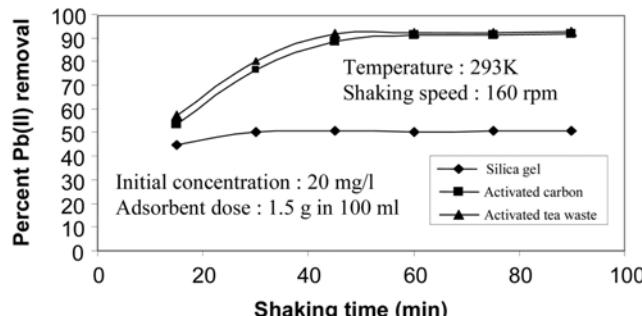


Fig. 2. Comparison study for selecting suitable adsorbent.

it is cheaper than activated carbon.

2. Characterization of Adsorbent

The activated tea waste was found to be stable in water, dilute acids and bases. The density and porosity were found to be 1.40 g/ml and 0.25 fraction, respectively. The total acidity and cation exchange capacity were found to be 3.01 and 0.87 meq/g. The presence of β -polyphenylene sulfide is indicated by the X-ray diffraction pattern of activated tea waste. The surface area obtained from the N_2 adsorption isotherm was found to be 480.16 m²/g.

The adsorbent behaves as neutral at pH zero change. To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pH_{PZC}) of the adsorbent. Adsorption of cation is favored at $pH > pH_{PZC}$, while the adsorption of anion is favored at $pH < pH_{PZC}$. The results are shown in Fig. 3. It is observed that the point of zero charge is 5.6 irrespective of difference of HNO_3 used. The physico-chemical properties of the adsorbent are summarized in Table 1.

3. Effect of Shaking Time

The time-dependent behavior of Pb(II) adsorption was measured by varying the time between the adsorbate and the adsorbent in the range of 15-90 min. Adsorption of Pb(II) vs. shaking time for known amount of adsorbent dose of 1.5 g is shown in Fig. 4. Fig. 4 reveals that the percent Pb(II) removal increases as the shaking time is in-

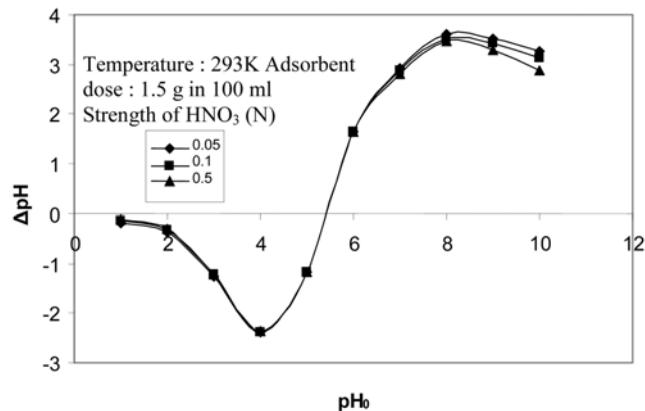


Fig. 3. pH of zero charge of activated tea waste.

Table 1. The main physico-chemical characteristics of adsorbent

Parameter	Value	
	Tea waste	Activated tea waste
Surface area (m ² /g)	495.54	480.16
Particle size (μ m)	200-250	200-250
Elemental analysis (%)		
C	57.6	54.2
H	8.25	7.75
N	0.42	0.37
O	33.1	30.2
S	0.52	7.43
Ash content (%)	4.83	2.52
Moisture content (%)	5.40	6.78
pH_{PZC}	6.2	5.6

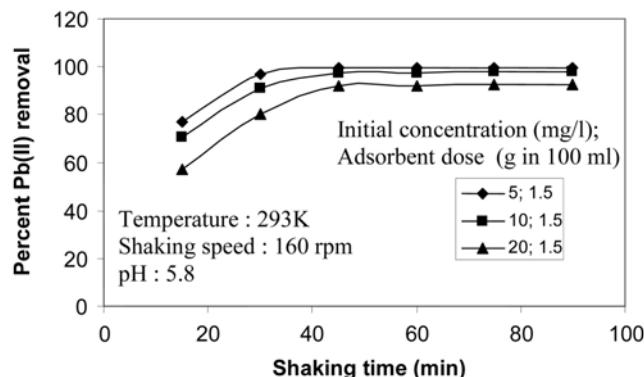


Fig. 4. Effect of shaking time on percent removal of Pb(II) by activated tea waste.

creased and attains equilibrium in 45 min, irrespective of Pb(II) concentrations (5-20 mg/l) and different adsorbent doses. The equilibrium time 45 min has been fixed for the rest of the batch experiments. The maximum amount of Pb(II) is removed with in the first 45 min. The maximum percent removal is found as 99.7, 97.9 and 92.5% at the initial concentrations of 5, 10 and 20 mg/l, respectively.

4. Effect of Particle Size

Adsorption is a surface phenomenon and the extent of adsorption is expected to be proportional to the surface area available for adsorption. The smaller the particle of adsorbent, the greater will be surface area and greater will be amount of adsorption accomplished per unit mass of the adsorbent.

In the present work, the effect of adsorbent particle size was investigated by using the average particle size (85, 115, 150, 235, 340, 405, and 510 μm) under identical conditions of initial concentration (5 and 20 mg/l), adsorption dose (1.5 g in 100 ml) and temperature (293 K). The pH of the solution was maintained at 5.8. The results are shown in Fig. 5. It is observed that removal of Pb(II) increases with decrease in the particle size of adsorbent used in the present investigation.

5. Effect of Adsorbent Dose

The effect of adsorbent dose on the percent removal of Pb(II) at various initial Pb(II) concentrations (5, 10, 15 and 20 mg/l) is shown

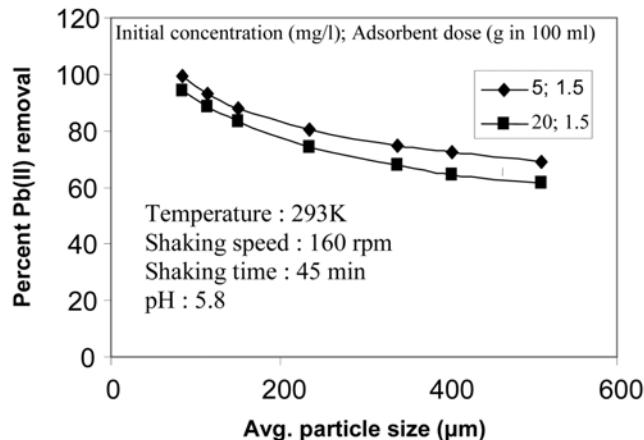


Fig. 5. Effect of particle size on percent removal of Pb(II) by activated tea waste.

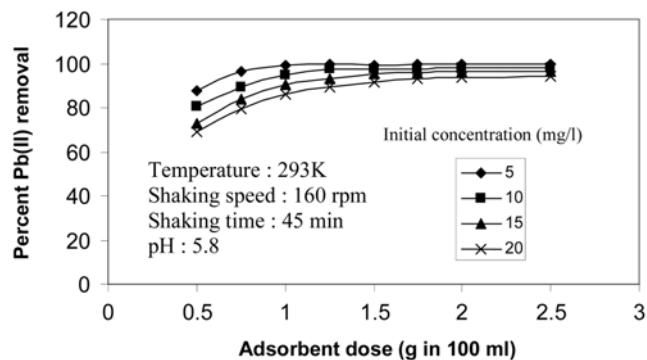


Fig. 6. Effect of adsorbent dose on percent removal of Pb(II) by activated tea waste.

in Fig. 6. To achieve the maximum adsorption capacity of the activated tea waste for Pb(II), the dose of tea waste was varied from 0.5 to 2.5 g/100 ml.

Other parameters like temperature (293 K), average particle size (85 μm), shaking speed (160 rpm) and a pH of 5.8 were kept constant. The experimental results reveal that percent Pb(II) removal increases with increasing adsorbent dose and then reaches the maximum removal at a particular amount of adsorbent. After that, the removal is not changed with the adsorbent dose showing that the condition of equilibrium is established. It is evident that the amount of adsorbent doses required to achieve the maximum removal of 99.3, 97.8, 96.1 and 93.8% is 1.0, 1.25, 1.75 and 2.0 g for the concentrations of 5, 10, 15 and 20 mg/l, respectively.

6. Effect of Initial pH

Waste water treatment using conventional and nonconventional adsorbents is highly dependent on the pH of waste water under treatment, as it may affect the surface charge of adsorbents as well as the degree of ionization of different pollutants. The acidity of solution (pH) is one of the most important parameters controlling uptake of heavy metals from waste water. The adsorption of lead was studied over a pH range of 1.0-7.0 and the results are given in Fig. 7. From Fig. 7, it is observed that the removal of Pb(II) increases as the initial pH is increased and attains a maximum value at pH 5.8. After that, it decreases very slowly up to the pH of 7.0. The decrease of the adsorption at higher pH may be attributed to the hydrolysis of Pb(II) in the solution, and therefore the separation may not be due to ad-

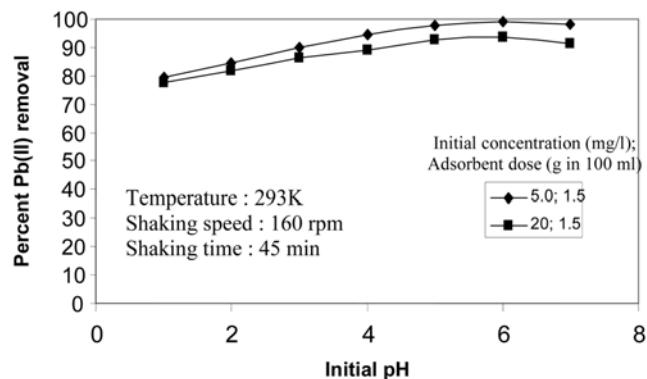


Fig. 7. Effect of initial pH on percent removal of Pb(II) by activated tea waste.

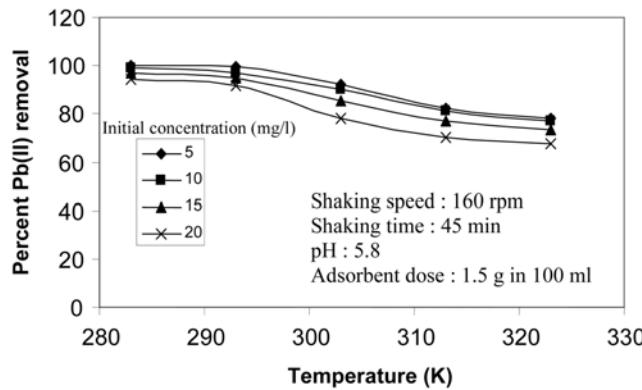


Fig. 8. Effect of temperature on percent removal of Pb(II) by activated tea waste.

sorption. Similar behavior has been reported by Gupta and Ali [2] for the adsorption of lead.

7. Effect of Temperature

As temperature can influence the final value of adsorption, therefore, the study of its effect on the adsorption process becomes an important aspect in waste water treatments. Effect of temperature on equilibrium capacity for adsorption is defined as heat of adsorption. Adsorption reactions are normally exothermic and the extent of adsorption in most of the cases decreases with increasing temperature [18]. Decrease in the adsorption with increase in temperature may be explained on the basis of rapid increase in the rate of desorption of the adsorbed species from the surface of the adsorbent [20].

The effect of temperature on the adsorption of Pb(II) has been studied by varying the temperature from 283 to 323 K under identical conditions. The results are shown in Fig. 8. The results show that maximum adsorption occurred at 283 K for Pb(II) ions and it also decreased at higher temperatures irrespective of concentration of Pb(II). The order of the adsorption for Pb(II) ions was 283>293>303>313>323 K. The increase in adsorption with decrease in temperature indicates exothermic nature of adsorption process.

8. Effect of Foreign Ions

Real waste water contains various ions such as Ca(II), Mg(II), Na(I), K(I), SO_4^{2-} , Cl^- and NO_3^- . The effect of these ions was, therefore, investigated to see the removal efficiency of activated tea waste on adsorption of Pb(II). The percent Pb(II) removal was found to decrease from 2.0 to 8.7 in the presence of above mentioned foreign ions (Table 2). The results show a non-selective nature of adsorbent for removal of Pb(II) ions in presence of other interfering ions.

Table 2. Effect of foreign ions on percent removal of Pb(II)

Foreign ions	% Decrease in removal of Pb(II)
Ca(II)	6.9
Mg(II)	5.8
Na(I)	8.7
K(I)	7.5
SO_4^{2-}	3.0
Cl^-	3.6
NO_3^-	2.0

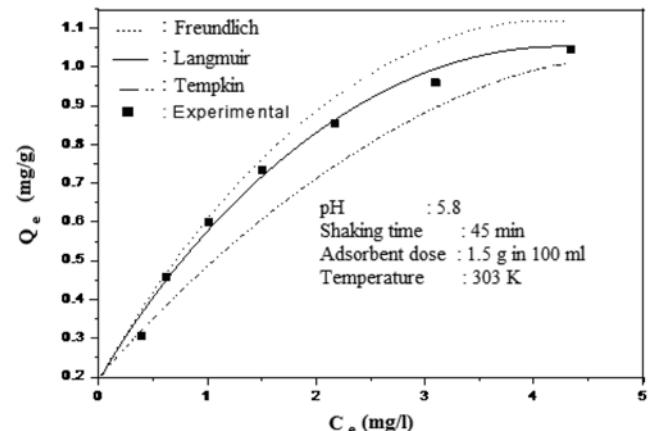


Fig. 9. Comparison of the experimental (legends) and the plots of Langmuir, Freundlich and Tempkin (lines) isotherms for the adsorption of Pb(II) onto activated tea waste at 303 K.

9. Adsorption Isotherms

Analysis of equilibrium data is important for developing an equation that can be used to compare different adsorbents under different operational conditions and to design and optimize an operating procedure. Batch experiments were, therefore, performed to obtain equilibrium adsorption data for the adsorbent - adsorbate system investigated in this work. The equilibrium data for activated tea waste was obtained under identical condition of experimentation and analyzed by the well known Langmuir, Freundlich and Tempkin isotherm models [21-23].

The experimental isotherm determined at 303 K is presented in Fig. 9. It can be seen that the adsorption isotherm exhibits an H-shape, which corresponds to the classification of Giles et al. [24]. The H-shaped isotherm is characteristic of the cases of high affinity of solute for an adsorbent. Such isotherm indicates that there is no competition from the solvent for adsorption sites. Several isotherm equations have been used for the equilibrium modeling of adsorption. Out of these isotherm equations, three have been applied for this study, the Langmuir, Freundlich and Tempkin isotherms:

$$\text{Langmuir: } \frac{C_e}{Q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (3)$$

$$\text{Freundlich: } \ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

$$\text{Tempkin: } Q_e = B \ln A + B \ln C_e \quad (5)$$

where Q_e is the equilibrium amount adsorbed (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l), Q_0 and K_L are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. K_F and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. A , B and Z are the Tempkin constants. The constant $B (=RT/Z)$ determines the heat of adsorption. The estimated parameters of these models have been evaluated by regression analysis and the results are shown in Table 3.

To compare the validity of isotherm equations more definitely, a normalized standard deviation, ΔQ (%) is calculated as follows:

Table 3. Isotherm constants and normalized standard deviation (ΔQ , %) for the adsorption of Pb(II) onto activated tea waste at 303 K

Isotherm constants	Magnitude
Langmuir	
Q_0 (mg/g)	1.3510
K_L (l/mg)	0.7890
R^2	0.9995
ΔQ (%)	7.6
Freundlich	
K_F	1.8010
n	2.010
R^2	0.9853
ΔQ (%)	16.7
Tempkin	
A	1.7770
B (l/mg)	0.3716
Z (J/mol)	7227.09
R^2	0.9690
ΔQ (%)	21.5

$$\Delta Q (\%) = 100 \times \sqrt{\frac{\sum [(Q_e^{exp} - Q_e^{cal})/Q_e^{exp}]^2}{N-1}} \quad (6)$$

Where the superscripts 'exp' and 'cal' show the experimental and calculated values and N is the number of measurements. The validity of the isotherm models is tested by comparing the experimental and calculated data at 303 K (Fig. 9). ΔQ (%) values given in Table 3 show the applicability of the Langmuir model. The adsorption data of Pb(II) onto activated tea waste were found to fit well with the Langmuir equation, while the Freundlich and Tempkin equations did not fit the adsorption data well. This is also confirmed from the data of correlation co-efficient (R^2). The correlation co-efficient for the Langmuir equation is high (Table 3).

10. Kinetic Analysis

The effect of temperature on adsorption of Pb(II) by activated tea waste can be explained on the basis of thermodynamic parameters, i.e., change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The expressions of these thermodynamic parameters are given below:

$$\Delta G^\circ = -RT\ln K_L \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

$$\ln K_L = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (9)$$

The value of ΔG° was calculated as -3.72, -3.49 and -3.45 kJ/mol at 303, 313 and 323 K, respectively. Free energy increases with increased temperature, indicating a decrease in adsorption at higher temperature, i.e., exothermic nature of adsorption. The values of ΔS° and ΔH° were found as -86.58 kJ/mol and -284.18 J/mol·K, respectively. The negative value of ΔS° reflects that no significant change occurs in the internal structure of activated tea waste during the adsorption of Pb(II).

The kinetic analysis is quite significant in waste water treatment as it describes the solute uptake rate which in turn controls the residence time of solute uptake at the solid-liquid interface. Temperature, adsorbent dose and shaking speed were kept constant for all experiments. To evaluate the adsorption kinetics of Pb(II) ions, the first-order and second-order kinetic models were tested. The Lagergren pseudo first-order kinetic model is generally expressed as follows [25]:

$$\log(Q_e - Q) = \log Q_e - k_f t / 2.303 \quad (10)$$

where Q_e is the amount adsorbed (mg/g) at equilibrium, Q is the amount adsorbed (mg/g) at time t and k_f the adsorption rate constant (min^{-1}).

The pseudo-second order model can be expressed as:

$$t/Q = 1/k_s Q_e^2 + t/Q_e \quad (11)$$

where k_s is the adsorption rate constant (g/mg·min). The results obtained for adsorption of Pb(II) were fitted to Eq. (11). A pseudo-second-order model provides better correlation than first-order model. The kinetic parameters calculated are given in Table 4. The rate constant decreases with initial Pb(II) concentration. At high concentration the difference between the concentration Pb(II) ion in the bulk of the liquid and that at solid-liquid interface (driving force for adsorption) is high, and therefore higher adsorption capacities are obtained at higher Pb(II) concentrations.

The rate constant for intraparticle diffusion (k_d) is given as [26]:

$$Q = k_d t^{1/2} \quad (12)$$

Where k_d is in $\text{mg/g} \cdot \text{min}^{0.5}$. The rate constant (k_d) decreases with increase in initial Pb(II) concentration (Table 4). The data points of Q vs. $t^{1/2}$ for all initial Pb(II) concentrations have a similar general trend, i.e., initially curved part, followed by a linear part and then a plateau. The initial curved part may be attributed to the bulk diffusion, the linear part to the intraparticle diffusion and the plateau to the equilibrium. This shows that Pb(II) ions transfer from bulk of the liquid to solid-liquid interface and then from the solid-liquid interface to the interior or the solid particles [27]. Both the transport of Pb(II) ions from bulk of the liquid to interior of the solid and the adsorption of Pb(II) ions on the adsorption sites are responsible for the removal of Pb(II) ions.

Table 4. Kinetic parameters of Pb(II) on activated tea waste (T=293 K, adsorbent dose=1.5 g in 100 ml, shaking speed=160 rpm, pH=5.8)

Initial Pb(II) conc. (mg/l)	First-order kinetic model			Second-order kinetic model			Intraparticle diffusion	
	K_f (min ⁻¹)	Q_e (mg/g)	R^2	K_s (g/mg·min)	Q_e (mg/g)	R^2	K_d (mg/g·min ^{0.5})	R^2
5	0.019	0.812	0.931	0.319	1.748	0.999	0.091	0.982
10	0.015	1.915	0.927	0.135	3.821	0.997	0.185	0.967
20	0.012	3.904	0.918	0.072	6.987	0.994	0.356	0.995

sible for the removal of Pb(II) ions by activated tea waste.

11. Comparison of Activated Tea Waste with other Adsorbents

Many researchers have experimented with various waste materials as low cost adsorbents for Pb(II) removal. Good results were obtained by various researchers where lead was efficiently removed by various waste materials. Comparisons of the adsorbents are difficult because of inconsistencies in data presentation [28]. However, from the literature reviewed, the adsorbents used by various workers were compared in terms of maximum percent removal of Pb(II). By comparison of the results obtained from this study to the previously reported work (Table 5) on removal of Pb(II) ions, it can be stated that activated tea waste is equivalent or superior to other adsorbents reported in literature.

12. Column Study Results

Adsorption column capacity at 50% breakthrough expressed in mg of Pb(II) adsorbed per g of adsorbent was calculated using Eq. (13):

$$\begin{aligned} \text{Adsorption column capacity at 50\% breakthrough} \\ = & [\text{Breakthrough time (at 50\%)} (\text{h}) * \text{flow rate (l/h)} \\ & * \text{feed concentration (mg/l)}] / \text{mass of adsorbent in bed (g)} \quad (13) \end{aligned}$$

Table 6 shows the column adsorption capacity for Pb(II) on acti-

vated tea waste for varying operating variables like bed height, flow rate and feed concentration. The column capacity for Pb(II) adsorption for the bed height of 0.4 m, hydraulic loading rate of $7.64 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$ and feed concentration of 5 mg/l for 50% breakthrough concentration was found as maximum of 0.497 mg/g. From comparison of adsorption capacity between batch and column experimental results, it was seen that the less stirred property as well as less residence time in column mode may reduce the Pb(II) adsorption capacity of activated tea waste.

CONCLUSIONS

The preliminary studies presented here show that activated tea waste is an effective adsorbent for removal of Pb(II) from aqueous solution. The optimum initial pH corresponding to maximum removal of Pb(II) by the adsorbent is 5.8, which is greater than pH_{PZC} of the adsorbent. Removal of more than 99.5% has been achieved under optimum conditions. The removal of Pb(II) decreased with increase in temperature. The adsorption equilibrium data was described well by the Langmuir equation and adsorption was found to be exothermic.

Adsorption capacities for column experiments were lower com-

Table 5. Comparison of Pb(II) adsorption onto activated tea waste and other adsorbents available in literature

Name of adsorbent	Maximum percent of Pb(II) removal	Optimum pH	Isothermal model fit	Thermodynamic parameters			Reference
				ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	
Activated carbon from coconut shell	99.0	4.5	Langmuir and Freundlich	-4.31	93.42	312.3	[4]
Activated phosphate	77.5	3.0	Langmuir and Freundlich	7.86	2.09	-19	[5]
Natural phosphate	57.6	4.0	Langmuir	3.15	57.28	179	[5]
Bagasse fly ash	98.0	6.0	Langmuir and Freundlich	-3.27	11.44	48.3	[2]
Palm shell	95.2	5.0	Langmuir	-	-	-	[29]
Activated carbon							
Red mud	88.2	4.0	Langmuir and Freundlich	-20.74	-85.94	-208	[3]
Carbon aerogel	96.8	5.5	Langmuir	-1.71	43.82	111.2	[30]
Olive cake	97.3	4.9	Langmuir and Freundlich	-15.86	44.53	199	[31]
Bentonite clay	98.0	3.4	Langmuir and Freundlich	-54.26	56.25	250	[7]
Tea waste	94	5.5	Langmuir and Freundlich	-	-	-	[16]
Activated tea waste	99.7	5.8	Langmuir	-3.55	-86.58	-248.18	Present study

Table 6. Fixed bed column adsorption capacity of 50% breakthrough concentrations at various operating conditions

Feed concentration (mg/l)	Breakthrough time, 50% (h)	Hydraulic loading rate (m ³ /h·m ²)	Bed height (m)	Adsorption column capacity (mg/g)
2.0	7.65	7.64	0.4	0.298
5.0	10.05	2.30	0.4	0.294
5.0	7.35	4.60	0.4	0.430
5.0	5.10	7.64	0.4	0.497
5.0	3.00	9.17	0.4	0.351
5.0	2.85	7.64	0.3	0.370
5.0	5.70	7.64	0.5	0.448
8.0	2.40	7.64	0.4	0.374
10.0	1.50	7.64	0.4	0.292

pared to batch experiments. The pseudo-second order model provides better correlation than the pseudo-first order model. The activated tea waste used in the present study is equivalent or superior to other absorbents reported in the literature. Activated tea waste showed its non-selective behavior during the removal of Pb(II) ions in the presence of other competitive ions present in real wastewater. The results clearly indicate that this system can be successfully used for the removal of Pb(II) from aqueous solution and waste water.

ACKNOWLEDGMENT

The author thanks Banaras Hindu University, India for providing financial support to undertake the work.

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