REMOVAL OF Pb(II) FROM AQUEOUS SOLUTION BY SORPTION ON USED TEA LEAVES

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ABSTRACT

Batch sorption study was performed using used black tea leaves (UBTL) as a low-cost adsorbent for the removal of lead (II) from aqueous solutions. Experiments were conducted as a function of contact time, initial metal ion concentration, solution pH and temperature. The sorption of Pb(II) on used tea leaves increases with increase of initial pH of solution upto a certain limit which corresponds to the pH nearly 5. The sorption isotherms follow Langmuir equation better than Freundlich equation. Again the Langmuir equation is more applicable at higher temperatures compared to those at low temperature at all pH. The monolayer sorption capacity decreases with increase in processing temperature but the overall sorbed amount increased with the increase in temperature at all pH. The positive value of estimated heat of sorption suggests the activated sorption. A probable mechanism of the sorption of Pb(II) on used tea leaves was proposed based on the surface charge of used tea leaves and the change of charge of Pb(II) with the pH of solution.

INTRODUCTION

Lead (II) is one of the highly toxic metal ions to the aquatic lives and human beings even at very low concentration. According to WHO, the permissible limit of Pb(II) in drinking water is 0.005 mg/L. All the compounds containing lead are considered as cumulative poisons that affect the gastrointestinal track, nervous system and sometimes both of biological system[1]. The chief sources of lead in water are the effluents of processing industries. Lead can enter the body through inhalation, and dermal contact with lead compounds. Upon reaching the blood stream, lead affect blood cells and the central nervous system. Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women. Fetuses and children under the age of seven and are most susceptible to lead poisoning, which has long-term and irreversible effects[2]. The symptoms of lead poisoning include headaches, poor appetite, trouble in sleeping, crankiness and vomiting.

Since the lead salts are widely used in industries; factories of batteries, paints, varnishes, solderings etc., the improper disposal of the wastes from these industries causes lead pollution in the environment. Various methods are currently used for removal of lead and other heavy metals from aquatic media including precipitation[3], coagulation[4], filtration[5], flotation[6,7], sedimentation[7], membrane process and electrochemical technique[8], ion-exchange[9] and adsorption[10-14] on solid. Many of these

methods require high capital and recurring expenditure; consequently they are not suitable for small-scale industries. At low concentration removal is more efficient by ion-exchange or adsorption on solid adsorbent. High capital and regeneration cost of activated carbon and ion-exchange resins have resulted in an increased search for low cost absorbent. In recent years, considerable attention has been devoted to the study of economical removal of Pb (II) from solution by sorption using agricultural materials such as rice husk[15], sugar beat pulp[10], clay soil[11], alfalfa biomass[12], lignite carbon[13], peat carbon[14] etc. Each method has merits and limitations in application. The present investigations revealed that the fresh and used tea leaves can be used as potential scavengers of heavy metal ions mainly Cr (VI)[16-17] and Cr (III)[18]. The present research has been carried out to investigate the capability of used tea leaves to remove Pb(II) from aqueous solution at different temperatures and varied pH. Thermodynamic parameters of sorption and its mechanism were also investigated.

EXPERIMENTAL

Preparation of Sorbent: Used black tea leaves (UBTLs) were prepared from Lipton TAAZA black tea leaves (Batch–03A, Manufacturing date: August 03, 2006). About 200 g of Lipton TAAZA tea leaves were added to about 700 mL of boiling distilled water. After 2 hours boiling of fresh tea leaves, leaves were washed with hot distilled water followed by cold distilled water for several times until the tea colour completely disappeared. After washing the tea leaves were initially dried at room temperature and eventually in an oven at 106 ^{0}C for 10 hours. Dried leaves were sieved through the metallic sieve of mesh size 0.25 mm and 0.30 mm. The resultant leaves in the range of 0.25 – 0.30 mm size were stored in an air-tight bottle for sorption experiments.

Analysis of Pb(II) Solution: 1000 mg/L stock solution was prepared by dissolving required amount of $Pb(NO_3)_2$ salt (A.G Merck, Germany) in double distilled water in a Teflon volumetric flask. Different concentration of Pb(II) solutions were prepared by required dilution of stock solution. Concentration of Pb(II) in solutions before and after of sorption were analyzed by Atomic Absorption Spectrophotometer (AAS) (Perkin-Elmer A.A analyst 800) using air acetylene flame and Hollow cathode lamp. The absorbance was measured at the most sensitive wavelength of 283.3 nm.

Determination of Optimum pH for Sorption Study: For the determination of optimum pH, 0.1 g of used tea leaves was taken in each of the ten bottles. 25 mL lead solution was taken in each bottle. The bottles were placed in a thermostatic mechanical shaker (SW B-20, Fions Ltd. Germany), maintained at 30°C and were shaken continuously for five hours. The reagent bottles were successively withdrawn after shaking for definite time and the solutions were centrifuged. After centrifuge the pHs of the solutions were measured. The difference of pH from the initial values was estimated as ΔpH. A plot of initial pH *vs* ΔpH, produces a curve which intersects the X-axis at a point as shown in Fig. 1.

Determination of Equilibrium Time: To determine the equilibrium time, 0.1g of used tea leaves was taken in 25 mL of 100 mg/L Pb(II) solution in each of a series of adsorption bottles. Before adsorption, pH of each bottle was maintained at pH 5.0 because this is the pH of 100 mg/L Pb(II) solution in double distilled water. The constant pH was obtained by drop-wise addition of 0.1 M HNO_3 or 0.1 M NaOH solutions whichever was necessary. The final pH of each solution was checked after sorption, which showed that the pH of the solution did not change by more than 0.2 units. All the bottles were shaken in a thermostated mechanical shaker. The bottles were taken out from the shaker after different time intervals. The solution from the sorption bottle was centrifuged and analyzed. The experiment was performed at 30°C. The amount sorbed *vs* sorption time plot is shown in Fig. 2.

Sorption Isotherms at Different Temperatures and pH: For the determination of sorption isotherm at 30°C and pH 4.0, 25 mL solution of various concentrations of Pb(II) ranging from 20 to 80 mg/L were taken in 7 bottles containing each of 0.1g used tea leaves and were shaken for 180 minutes, which was the equilibrium time as determined in previous section. After sorption for 180 minutes, the solution of each bottle was centrifuged and analyzed by AAS. Similar experiments were performed at 40 and 50 °C to obtain sorption isotherms at different temperatures and isotherms are shown in Fig. 3. Again, the experiments were repeated at pH 5.0 and 6.0 using temperatures of 30, 40 and 50 °C. The results are presented in Figs. 4 and 5, respectively.

RESULTS AND DISCUSSION

Determination of Optimum pH for Sorption Study

Before measuring the equilibrium time for the adsorption of Pb(II) on UBTLs it was important to determine the optimum pH of the solution to be used for sorption experiments. Fig. 1 shows the optimum pH is 5.3 at which minimum variation of solution pH during sorption process was observed. Optimization of solution pH is very important
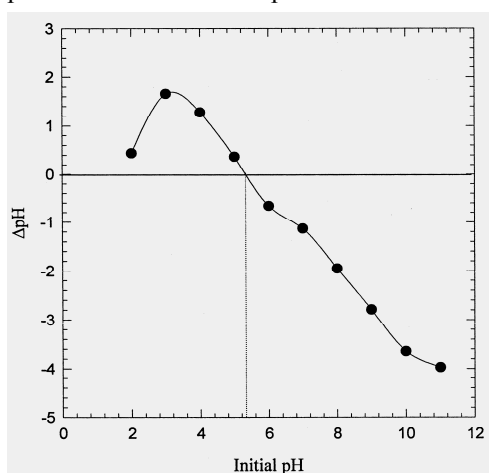

Fig. 1. Optimization of pH for the adsorption of lead (II) on UBTLs.

because if the solution pH is changed with sorption time it will be difficult to identify the sorption pH as well as the amount sorbed. During the determination of the effect of pH on sorption of lead on UBTLs, pH of solutions were varied from 4 to 6 where the initial pH of solutions did not change significantly after sorption.

Determination of Equilibrium Time

Equilibrium time is essential for sorption study to construct the sorption isotherm. Equilibrium time is a stage where sorption reached the saturation stage. Under the present experimental conditions, the equilibrium time for the sorption of Pb(II) on UBTLs was found to be 2 hours. Figure 2 shows that the change of sorbate concentration is negligible at equilibrium time, and it was also observed that the removal of Pb(II) on UBTLs is nearly 94.5%.
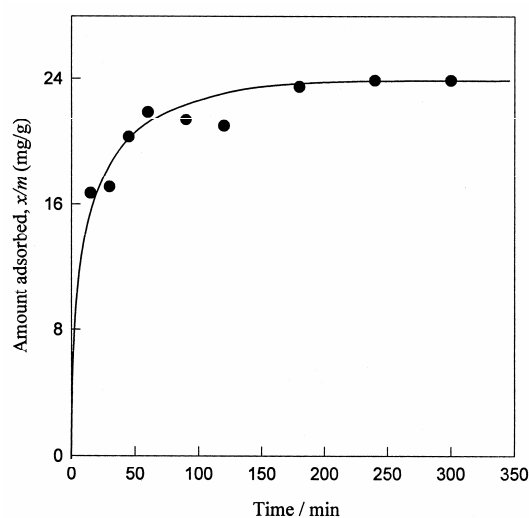

Fig. 2. Estimation of equilibrium time for the adsorption of lead (II) on UBTLs using pH 5.0 at 30.0 ± 0.5 °C.

Sorption Isotherm

Sorption isotherm is an important parameter for the characterization of an sorption process. In this study, sorption isotherms were determined at three different temperatures using solutions of three different pH values. Under all the experimental conditions the amount sorbed increases with the increase of equilibrium concentration. The sorption isotherms were obtained by plotting equilibrium concentration (C_e) *vs* amount adsorbed (mg/g) as shown in Figs. 3, 4 and 5, respectively for different values of pH and temperatures. Sorption isotherm follows Langmuir equation (Eqn. 1) [10] better than Freundlich equation (Eqn. 2) [11].

$$C_e/(x/m) = 1/q_m b + C_e/q_m \qquad\qquad (1)$$
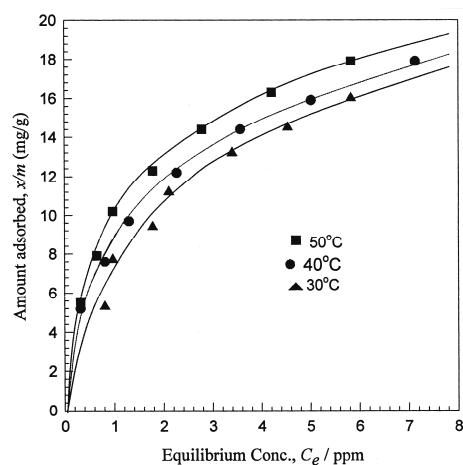$$\log x/m = \log k_F + 1/n \log C_e \qquad\qquad (2)$$

Fig. 3. Adsorption isotherms of lead (II) on UBTLs at different temperatures at pH 4.0.
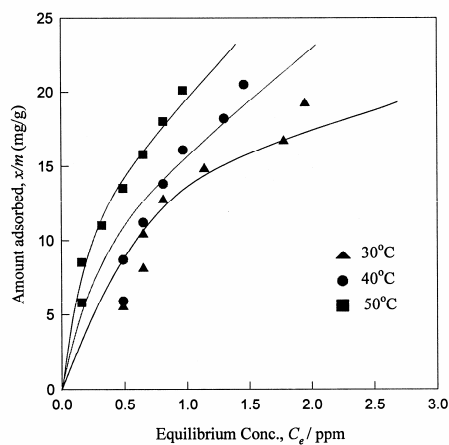

Fig. 4. Adsorption isotherms of lead (II) on UBTLs at different temperatures at pH 5.0
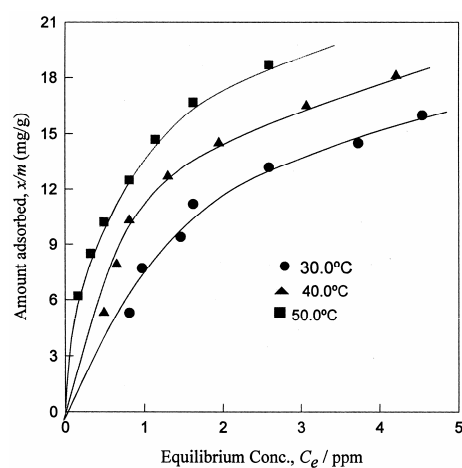

Fig. 5. Adsorption isotherm of lead (II) on UBTLs at different temperatures and at pH 6.0.

Here, C_e is the equilibrium concentration of Pb(II) in solution, x is the amount of Pb(II) sorbed on UBTLs, m is the amount of UBTLs used for sorption and k_F is Freundlich constant. Figs. 6-8 show that Langmuir equation is best fitted for the sorption of Pb(II) on used tea leaves at higher temperature compared with those of low temperatures in the range of 30–50 $^{\circ}$C. Langmuir constants at different temperatures and pH were calculated from Figs. 6-8 and given in Table 1. The maximum mono-layer sorption capacity evaluated from Langmuir constant (q_m) shows that pH 5 is suitable to obtain maximum mono-layer capacity. Table 1 shows that the maximum mono-layer capacity decreases with increase in sorption temperature at all pH values but the adsorption intensity constant, b increases with increasing sorption temperature. The adsorption isotherms (Figs. 3-5), and isobars (Fig. 9) show that the total sorption capacity at all pH values increases with increasing sorption temperature. Such types of observations suggest that the mono-layer sorption and chemical interaction both occurred simultaneously. The mono-layer sorption is due to physical forces. The increase in sorption with temperature suggests that the chemical interaction occurred with increasing temperature resulting the increase of adsorption intensity with temperature.
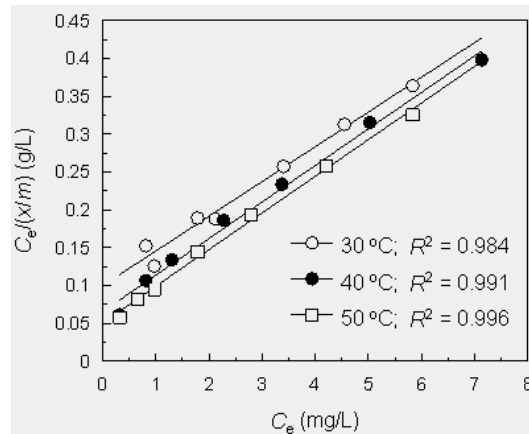

Fig. 6. Langmuir adsorption isotherm of Pb(II) on UBTLs at different temperatures and at pH 4.0.
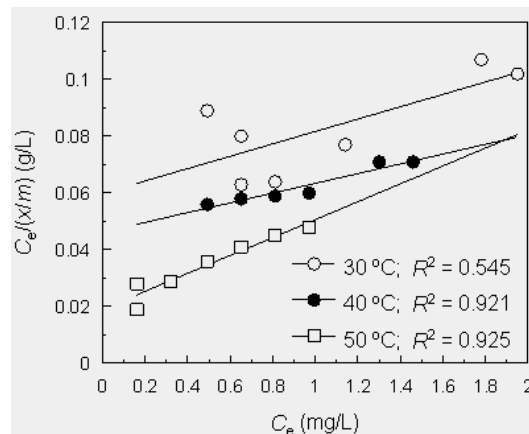

Fig. 7. Langmuir adsorption isotherm of Pb(II) on UBTLs at different temperatures and at pH 5.0.
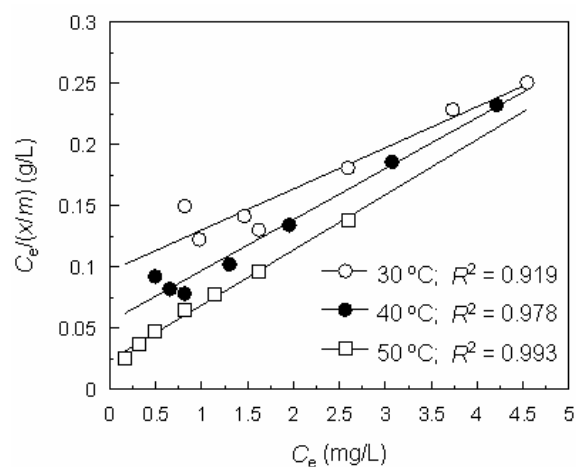
Fig. 8. Langmuir adsorption isotherm of Pb(II) on UBTLs at different temperatures and at pH 6.0.

Table 1.
Langmuir parameters for adsorption OF Pb(II) on used tea
leaves at different temperatures and PH

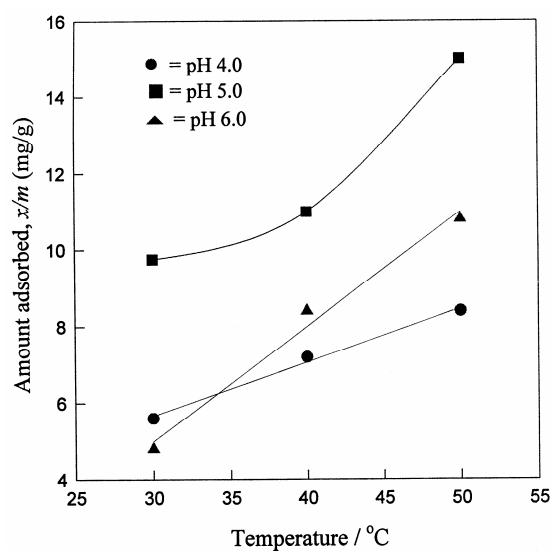| pH	q_m (mg/L) Temperature (°C)			b Temperature (°C)			R^2 Temperature (°C)		
	30	40	50	30	40	50	30	40	50
4.0	21.786	20.704	20.661	0.459	0.736	0.951	0.984	0.991	0.996
5.0	45.872	58.140	31.746	0.364	0.372	1.649	0.545	0.921	0.925
6.0	29.762	23.981	22.173	0.347	0.750	1.879	0.919	0.978	0.993

Fig. 9. Adsorption isobars for the adsorption of lead (II) on UBTLs at different pH.

Adsorption Isobar

To construct the adsorption isobar, the amount adsorbed at different temperatures under constant equilibrium concentration was estimated from different adsorption isotherms (Figs. 3, 4 and 5). Variation of amount adsorbed with temperature is presented in Fig. 9. Comparison of three isobars at different pHs in Fig. 9 shows that the adsorption increases with the increase of temperature over all pH values. Significant increase in amount adsorbed was observed at pH 5.0 throughout the range of temperature from 30 to 50 ^{o}C. Interestingly, when the pH of the solution was 4.0, the increase of adsorption slowed down .The pH$_{zpc}$ (zero point charge pH) of the surface of tea leaves is very close to pH 4.0 and the surface found almost neutral. At pH 5.0, surface is expected to be negatively charged that helps to adsorb Pb^{2+} ions. At pH 6.0, surface is more negative than before and sharp increase of adsorption is likely. But experimental results showed that the amount of Pb^{2+} removal is higher at pH 5.0 than pH 6.0.

Adsorption Isostere

To construct adsorption isostere, equilibrium concentrations at different temperatures under constant amount adsorbed (mg/g) were estimated from the adsorption isotherms (Figs. 3, 4 and 5). Fig. 10 shows a comparison of the variation in equilibrium concentration with temperature as an adsorption isosteric plot. Here the equilibrium concentration decreases with increase in temperature for all pH values over 4.0 to 6.0.
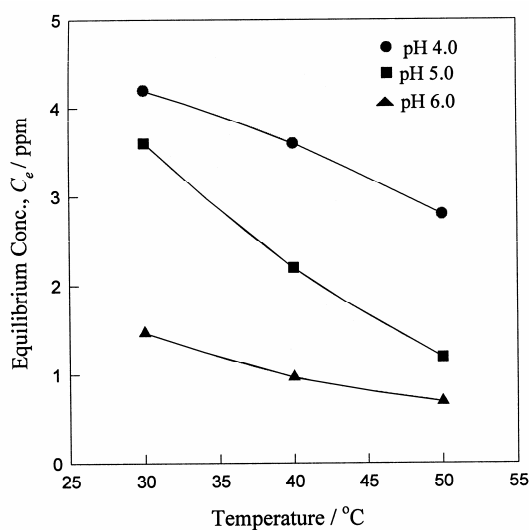

Fig. 10. Adsorption isosteres for the adsorption of lead (II) on UBTLs at different pH.

Sorption Thermodynamics

Thermodynamic parameters were determined from the findings of the effect of temperature on adsorption and using Equation (3).

$$\{\mathrm{d}\ln C_e / \mathrm{d}(1/T)\}_{\theta} = \Delta H_{ads} / R \qquad\qquad (3)$$

Where, θ indicates the fraction of surface coverage and ΔH_{ads} is the enthalpy of adsorption. For a particular amount adsorbed, the change of equilibrium concentrations with temperature have been calculated from Figs. 3, 4 and 5 for respective pH. Enthalpy of adsorption has been calculated from the slope ($\Delta H_{ads}/R$) of the linear plots $\ln C_e$ vs $1/T$ as shown in Fig. 11. The positive values of heat of adsorption vary from 20.22 to 44.71 kJ/mol. This shows the removal of Pb(II) ion from aqueous solution of pH over the range 4.0 to 6.0 is exothermic. Physisorption occur due to weak van der Wall force of attraction between the adsorbate and adsorbent. The adsorbed species lose their kinetic energy which is converted to heat energy. So the physisorption decreases with the increase of temperature.
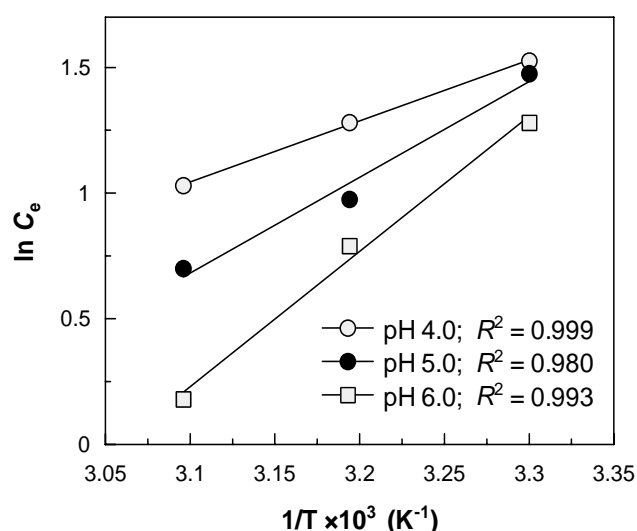

Fig. 11. A plot of $\ln C_e$ vs. $1/T \times 10^3$ for the adsorption of Pb(II) on UBTLs at different pH.

Effect of pH and Sorption Mechanism

The experimental results in Fig. 12, show that the amount sorbed depends largely on the solution pH. Generally, surface charge of adsorbent and also that of adsorbate are pH dependent. Pb(II) exists in acidic medium as free ions but at higher pH it precipitates as Pb(OH)$_2$. Hence the amount adsorbed and the mechanism of the adsorption is practically controlled by the solution pH.

Figure 12 shows that the amount adsorbed increases with the increase of pH from 4.0 to 5.0 and after this adsorption decreases with the increase of pH of the solution. Similar results were obtained during the investigations of removal of Pb(II) ion from aqueous medium using fresh tea leaves[19] rice husk[15], sago waste[20] and vermiculate[21].
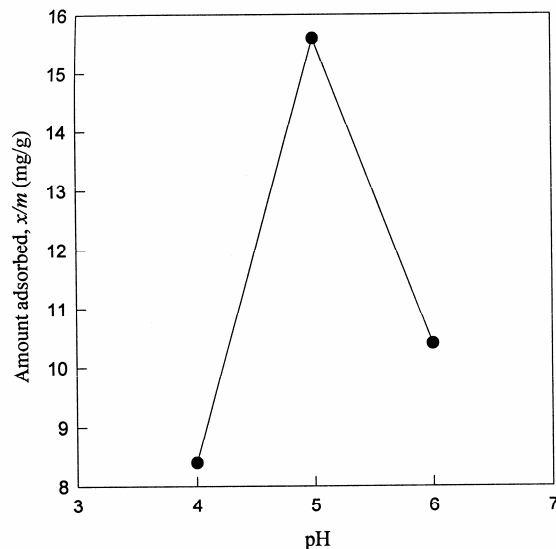
Fig. 12. Variation of amount sorbed with pH at constant equilibrium concentration at 30.0 ± 0.5 °C.

At low pH (4.0), the higher concentration of H^+ ions is present in the solution, which competes with the metal cation for exchange sites, and as such removal is less at pH below 4. Above this pH, the concentration of H^+ ion decreases where the concentration of metal ions remains constant, consequently the removal of metal increases at higher pH values. The removal of Pb(II) by ion exchange process at low pH values had been suggested by Tiemann *et al*[12] and Das *et.al*[21].

At pH 5.0, adsorption increases due to electrostatic force of attraction between negatively charged surface and Pb(II) ion. The electrostatic force of attraction arises due to the donation of lone pair of electron from oxygen atom of cellulosic material in tea leaves to Pb^{2+} ion. At higher pH (higher than 5), adsorption had been observed to decrease again. Similar observation was always found by Eligwe *et al*[13], and Khalid *et al*[15]. Pb(II) ion undergoes following reaction at pH 5.0[19].

$$Pb^{2+} + OH^- \rightarrow Pb(OH)^+ \tag{4}$$

$$Pb(OH)^+ + OH^- \rightarrow Pb(OH)_2 \tag{5}$$
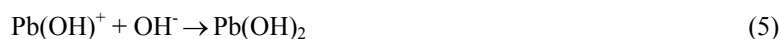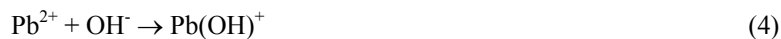
Eventually $Pb(OH)^+$ is also removed by electrostatic force of attraction of negatively charged surface. Reaction (5) suggests that Pb is also likely to be removed by precipitation reaction. Reaction (4) and (5) explains the significant increase of Pb^{2+} removal at pH 5.0. Further increase of pH of the solution to pH 6.0, causes the rapid reduction of Pb^{2+} removal. The following reactions may likely occur under this condition[19].

$$Pb(OH)_2 + OH^- \rightarrow Pb(OH)_3^- \qquad (6)$$

$$Pb(OH)_3^- + OH^- \rightarrow Pb(OH)_4^{2-} \qquad (7)$$

The anion thus formed cannot reach the negatively charged surface. This might be the reason of low adsorption at pH 6.0.

CONCLUSIONS

Used tea leaves act as a low-cost sorbent for the removal of Pb(II) from aqueous solution. The sorption is highly dependent on solution pH and temperature. The amount sorbed increases with increase of initial pH of the solution, and then decreases passing through a maximum. The maximum sorption corresponds to pH nearly 5.0. The sorption isotherms follow Langmuir equation better than Freundlich equation. Again the Langmuir equation is more applicable at higher temperatures than low temperature for all pH values. With the increase in sorption temperature over all pH values the monolayer adsorption capacity decreases but the adsorption intensity constant b increases. Again, from the adsorption isotherms, it has been noted that the total adsorption capacity increases with increase in sorption temperature over the range of pH used. Such observations suggest that the mono-layer adsorption is mainly due to physical forces. Chemical interaction occurs when temperature increases resulting the increase of adsorption intensity with temperature. Therefore, the total removal process is designated as sorption. The value of enthalpy of adsorption (ΔH_{ads}) was estimated to be 20.22, 30.40 and 44.71 kJ/mole at pH 4.0, 5.0 and 6.0 respectively. The enthalpy of adsorption increases with increase in solution pH and its positive value suggests the activated adsorption.

ACKNOWLEDGEMENTS

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