ADSORPTION OF Pb (II) IONS USED BLACK TEA WASTES FROM AQUEOUS SOLUTION

Dr. Tamara Kawther Hussien¹, *Nidaa Adil Jasim²

1) Lecturer, Environmental Engineering Department, Mustansiriyah University, Baghdad, Iraq.
2) Assist Prof., Highway and Transportation Department, Mustansiriyah University, Baghdad, Iraq.

Abstract: The present study investigates the possibility of removing lead (Pb II) ions from aqueous solution in batch process by the adsorption onto black tea wastes. The influences of different adsorption parameters such as pH, contact time, adsorbent dosage and metal concentration have been studied. The maximum result at optimum pH 4, 60 min contact time, 0.5 g/100ml dosage and 10 mg/l initial metal concentration were 96%, 98%, 97% and 98.5% respectively at room temperature. The equilibrium data depicted by Freundlich and Langmuir models. The Freundlich isotherm get together with the experimental data than Langmuir. This study enhance to use black tea waste as an inexpensive material, it can be an alternative to other expensive adsorbents used to remove Pb(II) ions from wastewater.

Keywords: Adsorption, Pb(II), Black Tea Wastes.

1. Introduction

Nowadays uncontaminated water becomes essential problem because many sources have been exhausted due to technological and industrial evolution [1]. Removal of heavy metals from wastewater becomes an important treatment because heavymetals are causing soil and water pollution [2]. Heavy metals have dangerous effects on human and animal health, they cannot be destroyed to a small extent so, they should been removed from water and soil [3].

Concentration of heavy metals that are discharged to the water and soil must be reduced before discharging, and the concentration must be reduced down to be fitted with the wastewater standard [4]. Lead is one of the heavy metals which is settled in
human and animal organs through air, water and food. Its maximum discharge limit is 0.5 mg/dm³ [4]. Its cumulative poisoning effects are serious cause hematological damage, anemia, kidney malfunctioning, brain damage, and severe lesions in liver, lungs, and spleen. Lead is a main raw material in batteries industry, fuel, pigments, photographic materials leaded glass. Refinery wastewater is considered a source of lead[5].

The removal of lead from polluted wastewater like the other kind of heavy metals is a problem over the worldwide. Coagulation-flocculation, chemical precipitation, ion exchange and flotation are the most conventional methods to remove or reduce lead from wastewater. May be there are many disadvantage for these methods like energy requirement, generation of toxic sludge[6]. Many researches improved that the adsorption method is an effective way and economic to treat wastewater polluted with heavy metals, because it is effective in separate the solute particles, low cost way, simple and excellent in removing contaminates from wastewater such as heavy metals [7, 8].

There have been many studies about removing of heavy metals like lead from industrial wastewater or mining waste effluents [9]. Chemical and biosorbents were used as an adsorbent, copper oxide was successful to remove Pb(II) ions in different conditions[10]. Plants leaves, seeds, tassel, were used to treat the wastewater polluted with Pb(II). A high percentage of Pb(II) was adsorbed onto maize tassel based activated [11]. Algae as a sort of biosorbent was investigated for the removal of Pb(II) ions from aqueous solutions [12]. Nano sorbents were employed to remove Pb(II) ions from polluted water such as nano-sized hydroxyapatite and carbon nano-tube [13, 14]. This study includes an evaluation of the effects of various operational parameters, such as pH, contact time, dosage of black tea wastes, metal concentrations on the Pb(II) ions adsorption process.

2. Materials and Methods

2.1. Adsorbate

Wastewater used in this experiment consists of heavy metals lead nitrate Pb(NO₃)₂. lead has a molecular weight of 207.2 g/mole. Pb(NO₃)₂ has a molecular weight of 331.23 g/mol were used for preparing synthetic solution. The desired concentration of Pb (II) was dissolved in deionized water of 3-8 micro S/cm conductivity. Solution pH was adjusted by adding 0.1 M HCL or 0.1 M NaOH and measured with pH meter type (3110, WTW, Germany). Mass of heavy metal salts added to water by assuming complete dissolution was calculated as follows equation:

\[ W = V \times C_i \times \frac{M \times W_t}{A \times W_t} \]  

(1)

where:
W: Weight of Pb(NO₃)₂ (mg).
V: Volume of solution (l).
Cᵢ: Initial concentration of lead ions in solution (mg/l).
M.wt: Molecular weight of Pb(NO$_3$)$_2$ metal salt (g/mol).
At.wt: Atomic weight of Pb$^{+2}$ ions (g/mole).

2.2. Preparation of Tea Wastes

The tea wastes used as adsorbent, the tea wastes were washed twice with distilled water to remove all excess and dried in oven for 24 hr at a temperature 60°C. the dried material was ground and sieved to get the particle size of 0.6 mm. Adsorbent characteristics were observed using scanning electron microscope (SEM), model AIS2300C(USA), Angstrom Advanced coated with gold. Fourier transform infrared spectroscopy (FTIR) analysis was done by [FT-IR spectrometer, BIOTECH ENGINEERING MANAGEMENT CO.LTD(UK)].

3. Experimental Studies

Lead samples were prepared by dissolving a known quantity of lead nitrate Pb(NO$_3$)$_2$ in distilled water and used as a stock solution and diluted to the required initial concentration (range from 10 to 50 mg/l). A sample of 100 ml of Pb (II) ions known concentration was added to each flask (250 ml) with a required amount of adsorbent and was agitated at a speed of 200 rpm in shaker (GEMMY orbit shaker, model VRN-480) at 25°C for a specified period of contact time, then the solution was filtered through a with filter paper (Whatman filter GF/C (0.45μm)). AA-6200 Atomic adsorption flame emission spectrometer (Shimadzu, Japan) was used to measure the remaining concentration of Pb$^{+2}$ ions. The percentage of removed Pb$^{+2}$ ions (removal efficiency $R\%$) was calculated by the different of the initial and equilibrium concentration of lead according to the following Equation:

$$R(\%) = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (2)$$

Where:
$C_o$ : initial concentrations of heavy metal (mg/l),
$C_e$ : final concentrations of heavy metal (mg/l).

4. Results and Discussion

4.1. SEM Figures

Figure 1 (L), shows the surface morphology of black tea wastes observed by scanning electron microscope before and after treatment process. From figure it is clear that the particles have small pores about 10 μm to allow more metal particles to accumulate on them by adsorption process, on the other hand, fig. 1 (R) clears the case after adsorption when these pores stuffed with metal particles to alter the surface to nearly smoothie.
4.2. FTIR Figures

FTIR spectra of Black tea waste before and after Pb (II) ions uptake are shown in Fig.2, respectively. FTIR spectra figure appears carboxylic, phenolic and hydroxyl groups that metal ions can react with them. Many crests were seen represent carboxylic group (3340 cm\(^{-1}\)), carboxylic group (1643 cm\(^{-1}\)), carboxylic acid group (1450 cm\(^{-1}\)), carboxylic acid group (1099 cm\(^{-1}\)) and aromatic group (825 cm\(^{-1}\)). These bands have moved to 3350 cm\(^{-1}\), 1631 cm\(^{-1}\), 1452 cm\(^{-1}\), 1097 and 823 cm\(^{-1}\). As a result, carboxylic and carboxylic acid groups were prevalent that take place in Pb(II) ions uptake [15]. However, hydroxyl group (2924 cm\(^{-1}\)), have not changed after the process, as shown in fig.2.
4.3. PH Results

The pH is a significant factor affecting the Pb (II) ions removal from waste water. Different values of pH were studied (2, 3, 4, 6, 8), at constant tea wastes dosage 1g/100 ml, contact time 120 min, speed 200 rpm at temperature 25°C, and metal concentration 50 mg/L.

The effect of pH on removal efficiencies of Pb (II) ions is shown in fig.3., the percentage of adsorption increases with increase in pH. The minimum adsorption was observed at low pH. This due to that the surface of the adsorbent becomes more positively charged at high H⁺ concentration such that pull force between black tea particles and metal cations is reduced. While, the negatively charged surfaces take a large area when pH increase, but, at very high pH the percentage removal decreases [16]. pH 4 was the optimum for subsequent experiments.

![Fig.3: Effect of pH on Pb(II) ions removal from solution.](image)

4.4. Contact Time Results

The percentage of Pb(II) ions adsorbed was estimated at different contact times (0 - 240) min keeping the other parameters fixed (pH4, tea wastes dosage1g/100 ml, T 25°C, initial concentration50 mg/L, and shaker speed 200 rpm).

Fig.4 shows the relation between the percentage removal efficiency of Pb(II) ions and different contact times. The results display the increasing in percentage removal rate with the time, however, after 60 minutes the adsorption rate took a constant rate without any advancement.

It can see that in the beginning of the run abundant in large surface area were available. As particles surface were saturated, the uptake rate is controlled by the rate of the metal particles are transported from the exterior to the interior sites of black tea particles [17]. Depending on these results 60 min was considered as the optimum time for the rest of the experiments.
4.5. Adsorbent Dosage Results

The impact of the adsorbent amount on the equilibrium adsorption for Pb(II) ions were investigated with black tea wastes of 0.1, 0.2, 0.5, 1, 2 and 3 g in six sets of 100 ml water, was contain Pb (II) ions concentration with 50mg/L, particle size 0.66 mm and pH 4. The samples were shaken for 60 min at speed of 200 rpm at room temperature. Samples were left in contact with adsorbent for 60 min, and then filtered with filter paper in order to analyze them. Fig.5 shows when the amount of adsorbent increased, adsorption of Pb (II) will increase, this is related to the increasing of large number of active surface area on the adsorbent when the adsorbent dosage increase [18]. Depending on these results 0.5 g/100 ml was considered as the optimum for the rest of the experiments, Many researches got similar results [19].

4.6. Initial Pb\(^{2+}\) ions Concentrations Results

In order to study the initial concentration effect, initial concentrations of Pb(II) ions were varied (10, 20, 30, and 50 mg/l), using tea wastes dosage 0.5g/100 ml at 60 min contact time, speed 200 rpm at 25\(^\circ\)C and at pH 4. Pb(II) ions analysis revealed that, the percentage removal was decreased from 98.6%-96% when metal ions concentration increased from 10 to 50 mg/l. Similar observation was reported in many works[20]. Fig.6 show In low concentration the removal efficiency is high, because the active
adsorbent particles sites are limited and they can uptake a small number of metal particles. However, at high metal concentration the adsorbent particles active sites are covered [21,22].

Fig. 6: Effect of initial concentration on Pb(II) ions removal from solution.

5. Adsorption Isotherm

Langmuir and Freundlich models were utilized to study the equilibrium process. The Langmuir model studies the homogenous surface adsorption. These models depend on three conditions: adsorption process works on monolayer only, every surface of his ability on the adsorption equality and the ability of active side to adsorb was changed from one to another, Langmuir model is [13]:

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(3)

where \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) is the amount adsorbed at equilibrium (mg/g), \( q_m \) is the maximum amount of adsorption on the adsorbent surface (mg/g) and \( K_L \) is the Langmuir constant (L/mg) related to energy adsorption capacity. Langmuir equation can be fitted with a straight line equation as follows [13]:

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \]  

(4)

The values of \( K_L \) and \( q_m \) were calculated from the slope of the line that is sketched between of \( C_e/q_e \) and \( C_e \). \( R_L \) and it is a constant represent if the adsorption is favorable, and it calculated from the following: [13]:

\[ R_L = \frac{1}{1 + K_L C_o} \]  

(5)

where \( C_o \) is the initial Pb(II) concentration (mg/L). The favorable adsorption when \( R_L \) values between 0 and 1

The linear plot of the Langmuir isotherm for Pb (II) adsorption is shown in fig. 7 and Table 1 respectively. From Table 1, the maximum adsorption capacity, \( q_m \) are
found 39.84 mg/g. $R_L$ value is 0.953, $K_L$ obtained value is 0.0049 l/g, the lower value of $K_L$ mean that the particle radius of black tea waste was small towards adsorption.

Freundlich equation studies the heterogeneous surface adsorption. The Freundlich model can be written as follows [21]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$ \hspace{1cm} (6)

where $q_e$ is adsorbed per unit mass of adsorbent (mg/g), $C_e$ is the concentration of adsorbate at equilibrium (mg/l), $K_f$ represent the adsorption capacity and $n$ is the intensity factor of the adsorption process. Intuitively $1/n$ is ranged between 0 to 1, and when the fraction is approach to 1, this mean the adsorption is favorable. $K_f$ and $1/n$ represent the slope of line that is sketched between $\ln q_e$ and $\ln C_e$ (fig.8). Table 1 shows Freundlich parameters. $R^2$ is equal to 0.995.

These results are fitted with both Langmuir and Freundlich models, however, $R^2$ result that obtained from Freundlich is little more than Langmuir model, so the uptake of Pb (II) onto black tea wastes is on heterogeneous layer [11].
Table 1: Isotherm main constants for removal of Pb (II) onto black tea wastes

| Adsorbent                 | Langmuir model | Freundlich model |
|---------------------------|----------------|-----------------|
| Black tea wastes          |                |                 |
| Parameters values         |                |                 |
| q_m (mg/g)                | 39.84          | 0.0049          |
| K_L (l/mg)                | 0.953          | 0.980           |
| R_L                       | 0.980          | 1.021           |
| R^2                       | 0.995          | 0.199           |
| K_f                       | 0.995          | 0.995           |

6. Conclusions

Black tea wastes have a good capacity of adsorption for Pb(II) ions. pH, contact time, adsorbent dosage, and adsorbate concentration, were essential factors in this study. The maximum adsorption capacity was found at pH 4, contact time 60 min, adsorbent dosage 0.5 g, and initial adsorbate concentration 10 mg/L, the maximum amount of adsorption was 39.4 mg/g with Langmuir model and the adsorption was favorable (R_L = 0.953), R^2 for Langmuir and Freundlich models were 0.98 and 0.995. This material can be successfully used as an environment friendly product for removal of heavy metals including heavily contaminated waters.

7. References

1. Mackenzie L. D., and David A. C., (2008), “Introduction to Environmental Engineering”. McGraw. Hill international edition. 4th.
2. Muhammad, A. A., Abed, F. I, and Al-musawi, T. J ., (2014), “Bisorption of Pb(II) from aqueous solution by spent black tea leaves and separation by flotation”, Desalination and Water Treatment, Doi 10.1080 / 19443994. 982194.
3. Gray, N. F., (2005), “Water technology; an introduction for environmental scientist's engineers”, Second edition, Elsevier Butterworth-Heinemann.
4. World Health Organization (WHO), (2011), Guidelines for drinking water quality, 4th ed.(ISBN 978 92 4 154815 1).
5. Pramanik, S., Saker, S., Paul, H., and Chattopadhyay, P., (2009), “A new polymer with 2-methoxy-1-imidazolylazobenzene functionality for determination of lead (II) and iron (III)”, Indian Journal of Chemistry, Vol (48), P.P. 30-37.
6. Kargar, M., and Yahyaabadi, S., (2012), “Adsorption consideration of Ni^{2+}, Fe^{2+}, Cu^{2+}, Cr^{2+} and Co^{2+} by phosphate and its concentration from solution in isotherm models”, IJRRAS, Vol.10,3, March, P. 397-407.
7. Kurniawan, T. A., Chan, G. Y. S., Lo, W. H., and Babel, S., (2006), “Physico-chemical treatment techniques for wastewater laden with heavy metals”, Journal of Chemical Engineering Vol (118), P.P. 93-98.
8. Ghani, M., Hefny, M., and Chaghaby, G., (2007),“ Removal of lead from aqueous solution using low cost abundantly available adsorbents”: International journal of environmental science and technology, Vol. 4, No. 1, p.p. 67- 73.
9. Zahra, A., (2012), “Lead removal from water by low cost adsorbents: A Review“ , J. Anal. Environ. Chem. Vol. (13), No.(1), p.p 1-08.
10. Farghali, A. A., Bahgat, M., Enaïet Allah, A. , and Khedr, M. H., (2013), “Adsorption of Pb(II) ions from aqueous solutions using copper oxide nanostructures“, beni-suef university journal of basic and applied sciences Vol.2 pp 61 -71.
11. Mambo, M., Linda, Ch., Benias, Ch. N., and Upenyu, G., (2013), “Adsorption Batch Studies on the Removal of Pb(II) Using Maize Tassel Based Activated Carbon“, Journal of Chemistry, Vol. 2013, Article ID 508934, pp 1-8

12. Naser, J., and Zoreh, S., (2012), “Removal of Pb (II) Ions from Aqueous Solutions by Cladophorarivularis (Linnaeus) Hoek“, The Scientific World Journal, Vol.2012, Article ID 793606, pp1-6.

13. Ramesh, S.T., Rameshbabu, N., Gandhimathi, R., Srikanth K. M., and Nidheesh, P. V., (2013), “Adsorptive removal of Pb(II) from aqueous solution using nano-sized hydroxyapatite“, Appl Water Sci Vol. (2013) 3, pp105–113.

14. Ahmed A. M., Ali M. R., and Noor A. H., (2016), “Adsorptive Removal of Lead Ions from Aqueous Solution Using Biosorbent and Carbon Nanotubes“, American Journal of Materials Science, Vol. 6(5), pp115-124.

15. Xiaoping Y., and Xiaoning, C., (2013), Adsorption Characteristics of Pb (II) on Alkali Treated Tea Residue, Water Resources and Industry Vol.3, pp 1–10.

16. Onundi, Y. B., Mamun, A. A., AKhatib, M. F., and Ahmed, Y. M., (2010), “Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon“, Int. J. Environ. Sci. Tech., Vol 7, No 4, p.p. 751-758.

17. Qassim, F.M., (2013), “Removal of Heavy Metal from water by Sorptive Flotation“, M.Sc., thesis, College of Engineering, University of Baghdad.

18. Heidari, A., Younesi, H., and Mehraban, Z., (2009), “Removal of Ni (II), Cd (II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nanomesoporous silica“, Chem. Eng. J. Vol. 153, p.p. 70–79.

19. Amiri, M. J., Fadaei, E., Baghvand, A., and Ezadkhasty, Z.,(2014), “Removal of Heavy Metals Cr (VI), Cd (II) and Ni (II) from Aqueous Solution by Bioabsortion of Elaeagnus Angustifolia “. J. Environ. Res., Vol 8(2):pp 411-420.

20. BalaraK1, D., Azarpira, H., and Mostafapour, F. K. (2016). “Thermodynamics of removal of cadmium by adsorption on Barley husk biomass“, Der PharmaChemica, Vol 8(10)pp 243-247.

21. Parmar, K., (2013), “Removal of cadmium from aqueous solution using cobaltsilicate precipitation tube (cospt) as adsorbent“, Inter national journal of science invention today, Vol 2(3), pp204-215.

22. Sayed, G., Dessouki, H. A. and Ibrahim, S. S., (2010), “Biosorption of Ni (II) and Cd (II) ions from aqueous solutions on to Rice Straw“, J Chem. Sci., Vol. 2, p.p. 1-11.