Comparison of Adsorption Characteristics of Tea Waste Biomass Materials and Char of *MORINGA OLEIFERA* L. for the Removal of Pb (II) Ions from Waste Water of Battery Repair Business

Kyaw Zan Aung*, Thet Thet Han**

**e-mail: kyawzanaung8@gmail.com*

Abstract

Adsorption of Pb^{2+} ions from aqueous solutions onto tea waste and char of *Moringa oleifera* branch were studied by batch adsorption method. The effect of initial metal ion concentration, optimum pH, contact time and dose of adsorbent on the adsorption of Pb^{2+} ions was studied. The optimum initial Pb^{2+} ions concentration, optimum pH, contact time and dose of adsorbent of tea waste for the maximum removal efficiency were found to be 4 mgL^{-1}, pH:4, contact time:40 min and adsorbent dose 6 g respectively. For char of *Moringa oleifera*, maximum removal efficiency was obtained when the optimum initial Pb^{2+} ions concentration: 6 mgL^{-1}, pH: 4, contact time: 40 min and adsorbent dose 6 g. The removal efficiency for Pb^{2+} ions in battery repair business waste water by tea waste and the char of *Moringa oleifera* at optimum condition of pH, contact time and dose were found to be 27.73 % and 33.65 % respectively. The equilibrium data were satisfactorily fitted to Langmuir and Freundlich isotherms. Langmuir monolayer adsorption capacity for Pb^{2+} ions by tea waste and char of *Moringa oleifera* branch were found to be 0.0025mg $g^{-1}$and 0.0071 mg g^{-1}. The equilibrium parameter R_L values of tea waste (0< 0.3307 <1) and char of *Moringa oleifera* (0< 0.2642<1) from Langmuir isotherm showed that the adsorption process was favorable. The 1/n value for tea waste (0< 1.674>1) and char of *Moringa oleifera* (0< 0.874<1) from Freundlich isotherm pointed out that the removal of Pb^{2+} ions by using tea waste was cooperative adsorption and char of *Moringa oleifera* biosorbent was associated with chemisorption process. It can be concluded that tea waste and char of *Moringa oleifera* biosorbent can be used as an adsorbent for the removal of Pb^{2+} ions in aqueous solution and waste water.

Keywords : Tea waste ,char of *Moringa oleifera* , Pb^{2+} ions, Langmuir isotherm, Freundlich isotherm

Introduction

Lead is especially known to be the most toxic metal among heavy metals, even at low concentrations in the aquatic environment. Current USEPA drinking water standard for lead is 15 μg L^{-1}, when present above 0.05 μg L^{-1} in drinking water, Pb^{2+} ions is a potent neurotoxic metal (Okoro and Ejike, 2007;Tasar, *et al*., 2014). Its target organs are bones, brain, blood, kidneys and thyroid glands. Biosorption is an alternative technology to remove heavy metal from dilute aqueous solutions based on the property of certain kinds of inactive and dead biomasses to bind and accumulate these pollutants. Biosorbent generally used for these purposes are wastes coming from agricultural and industrial activities or specially propagated biomasses of fungi, yeast and bacteria **(**Shima, *et al*., 2016). Heavy metal contamination is of worldwide environmental concern especially in developing countries. Conventional methods for removing heavy metals from industrial effluents (e.g. precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation) are often ineffective and costly when applied to dilute effluents. A good sorbent to remove heavy metal should be both

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*Professor,Dr.,Department of Chemistry,Myeik University

**Associate Professor,Dr.,Department of Chemistry,Myeik University

effective and inexpensive. Biosorption shows promise of fulfilling these requirements. The use of non-living biomass (biosorption) has been widely studied in the last years. It does not require nourishing and it does not suffer from toxicity problems (Volesky and Holan, 1995). Since non-living biomass behaves as an ion-exchange resin heavy metal bio-sorption appears to be effective technology for treatment of dissolved metals, especially in much diluted streams. It can be applied not only to remove toxic or radioactive metals, but also to recover precious metals. For instance, many kinds of seaweed and the microbial waste, coming from fermentation processes, are abundant and economic sources of biomass (Erdem *et al.* , 2013). This work investigates and compares the potential of commonly available waste biomass material such as tea waste and agriculture product such as *Moringa oleifera* branch in Myeik, Taninthari region which were used for removal of lead ions from aqueous solution and battery waste water. In this study the use of *Moringa oleifera* branch as a precursor for the preparation of char. The adsorption characteristics of tea waste were compared with the char of *Moringa oleifera*. Batch experiment was conducted to determine equilibrium data and the adsorption capacities for Pb^{2+} ion from aqueous solution. The effects of initial Pb^{2+} ion concentration, solution pH, contact time and adsorbent dosage on Pb^{2+} ion adsorption onto tea waste and char of *Moringa oleifera* were investigated. Adsorption isotherm and parameter which govern the adsorption process were also studied and reported.

Materials and Methods

Preparation of the Adsorbent

Tea waste was obtained from tea house in Myeik city. Soluble and colored components were removed from the biomass by washing with hot water at 85 ºC. This was repeated until the water was virtually colorless. The tea waste was oven dried for 12 hrs at 85 ºC. *Moringa oleifera* branch was collected from Myeik city and then it was washed thoroughly and then dried in an air for 72 hours to constant weight. The dried samples were cut into small pieces and made to charcoal by heating at 600^{o}C in Muffle Furnace for the period of 3 hours. The char produced was cooled to room temperature. The dried materials of tea waste and char of *Moringa oleifera* were grinded , sieved 40mesh siz**e** and stored in sealed polythene bags.

Preparation of Pb^{2+} Ion in Aqueous solution

Pb^{2+}ion was prepared from the stock solution of 1000 mgL^{-1} $Pb(NO_3)_2$. Reagents used were of analytical grade and deionized water was used in solution preparation. Other concentrations (2 - 10 mgL^{-1}) were obtained from this stock solution by serial dilution. The removal amount for Pb^{2+} ion in aqueous solution was analyzed by complexometric titration.

Batch Adsorption Experiment

Batch adsorption method was carried out on the adsorption of Pb^{2+} ion by tea waste and char of *Moringa oleifera*. The adsorption experiments were carried out in 250ml conical flasks with stopper on a shaker at 100 rpm and ambient temperature. The pH of the solution was adjusted to the desire pH by addition of 0.1M HCl or 0.1M NaOH and pH meter was used for pH measurement. The effect of initial metal ion concentration (2,4,6,8 and 10 mgL^{-1}), pH (2, 4, 6, 8 and 10), contact time (10, 20, 30, 40 ,50and 60 minutes) and adsorbent dose (1,2,3,4,5,6 and 7g) on removal efficiency for Pb^{2+} ion in aqueous solution by tea waste and char of *Moringa oleifera* were determined. During the experiment, one parameter considered was varied while the other three were remain constant. Sample solutions were withdrawn and filtered using

Whatman filter paper. The concentrations of Pb^{2+} ion solution before and after adsorption were determined using complexometric titration. For equilibrium studies, the experiment was carried out for 60 minutes to ensure that equilibrium was reached. The amount of adsorbate q_t, (in terms of mg g^{-1}) at time (t) was calculated using equation (1)

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

Where, C_o and C_t are the initial and the final metal ion concentration (mg L^{-1}), in

aqueous solution ,respectively; V is the adsorbate volume,(L) and m is the mass of adsorbent (g) (Ogunleye *et al*. ,2014). The amount of adsorbate q_e, (in terms of mg g^{-1}) at equilibrium was calculated by using equation (2)

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

Where, C_o and C_e are the initial and the final or equilibrium metal ion concentration (mg L^{-1}) in aqueous solution, respectively; V is the adsorbate volume,(L) and m is the mass of adsorbent used (g) (Ogunleye *et al*. ,2014). The removal percentage of metal ion from aqueous solution was calculated by using equation (3),

$$\%\,\text{removal} = \frac{(C_0 - C_t)\times 100}{m} \qquad (3)$$

Results & Discussion

Physicochemical Properties of Tea Waste and Char of *Moringa oleifera*

Physicochemical properties, such as pH, moisture content, bulk density, carbon content, volatile matter content and ash content of biosorbent were investigated. The data were inserted in Table 1.

Table1. Physicochemical Properties of Tea waste and Char of *Moringa oleifera* Biosorbent

Sample	pH	Moisture content (%)	Bulk density (g mL^{-1})	Ash content (%)
Tea waste	4.02	3.32	0.286	3.1
Char of *Moringa oleifera*	4.05	4.95	0.107	2.8

The moisture content of tea waste was less than the char of *Moringa oleifera* .The lower value of bulk density for char of *Moringa oleifera* pointed out that the char of *Moringa oleifera* have larger porosity than tea waste. It is confirmed that char of *Moringa oleifera* being more porous nature and may have the ability to take up more moisture than tea waste (Aziza *et al*., 2008)

Surface Morphology

Scanning electron micrograph (SEI) images *oleifera* are shown in Figure 1(a) and (b) of the tea waste and char of *Moringa*.

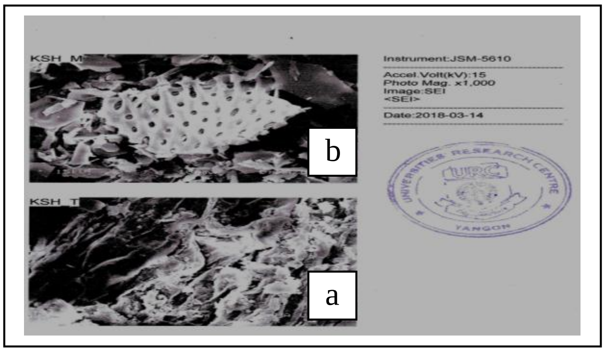


Figure 1. Secondary electron image of (a) tea waste and (b) char of *Moringa oleifera*

As can be seen from Figure 1(a), the Tea waste had a smooth surface, large particles, a compacter configuration and low porosity. In contrast, char *of Moringa oleifera* has the rougher surface, highly porous or large number of cavity in nature, is shown in Figure 3.1(b). The structure of char of *Moringa oleifera* exhibited irregular netlike structure, which implied the formation of complete three dimensional porous inner structures consisting rough surface texture. These characteristics signified that char of *Moringa oleifera* was more suitable for adsorption than tea waste.

Removal for Pb^{2+} Ions by Tea Waste and Char of *Moringa oleifera* from Aqueous Solution

The removal efficiency for Pb^{2+} ions from aqueous solution by tea waste and char of *Moringa oleifera* were studied by batch method.

Effect of initial concentration for Pb^{2+} ions

The effect of initial ion concentration on the adsorption capacity of Pb^{2+} ions onto tea waste and char of *Moringa oleifera* is as presented in Figure 3. The initial concentration of Pb^{2+} ions were varied from 2 mg L^{-1} to 10 mg L^{-1} and all other experimental variables such as pH 4, dose of biosorbent 3g, contact time 30 minutes and agitation speed 100 rpm were kept constant. The percentage removal of Pb^{2+}ions increased with initial concentration of Pb^{2+}ions. For tea waste, the optimum removal efficiency for Pb^{2+} ions was obtained at initial Pb^{2+} ions concentration 4 mg L^{-1} and optimum removal efficiency for Pb^{2+} ions was 6.45 %. When an initial concentration of Pb^{2+} ions was higher than 4 mg L^{-1}, the incremental Pb^{2+} ions removal became very low. For char of *Moringa oleifera*, the optimum removal efficiency for Pb^{2+} ions was obtained at initial Pb^{2+} ions concentration 6 mg L^{-1} and optimum removal efficiency for Pb^{2+} ions was 11.21 %. When an initial concentration of Pb^{2+} ions was higher than 6 mg L^{-1}, the percentage removal efficiency for Pb^{2+} ions became very low. When the initial metal ion concentration increases, lower adsorption yield take place at higher concentration and this was due to the saturation of adsorption sites (Hana *et al*., 2006).

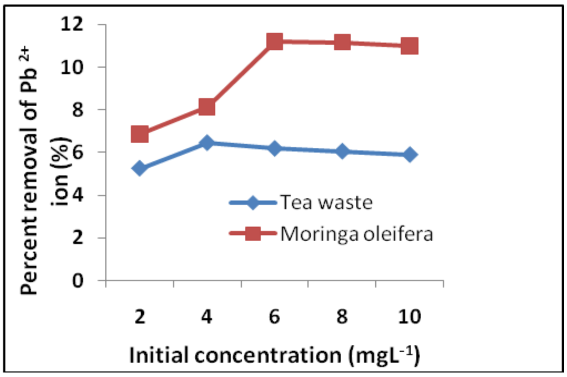


Figure 2. Effect of initial concentration of Pb^{2+} ions on removal efficiency of tea waste and char of *Moringa oleifera*

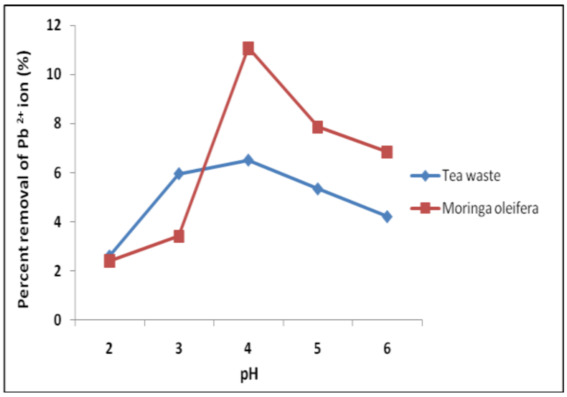


Figure 3. Effect of pH on the removal for Pb^{2+} ions by tea waste and char of *Moringa oleifera* from aqueous solution

Effect of pH

pH was an important parameter on biosorption of metal ions from aqueous solutions (Gong, 2005). Therefore, in order to determine the optimum pH for metal adsorption, the adsorption was studied at various pH. The results from the experiment work are as shown in Figure 3. The experimental results indicated that optimum value of pH was found to be 4.

Effect of contact time

The adsorption increases to specific time and becomes constant when equilibrium is reached. The contact time were varied from 10 min to 50 min and all other experimental variables such as pH, dose of biosorbent, agitation speed and concentration of Pb^{2+} ions for tea waste and char of *Moringa oleifera* were kept constant. The data is presented in Figure 4.

The experimental results indicated that a contact time of 40 min was sufficient to achieve equilibrium.

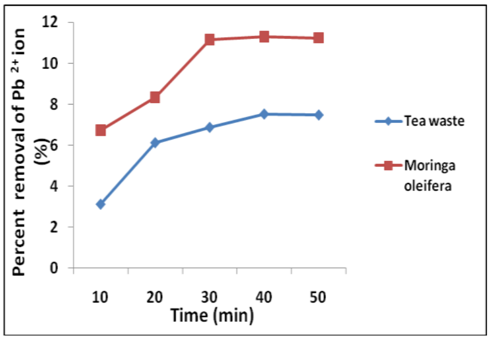


Figure 4. Effect of contact time on the removal efficiency for Pb^{2+} ion in aqueous solution by tea waste and char of *Moringa oleifera*

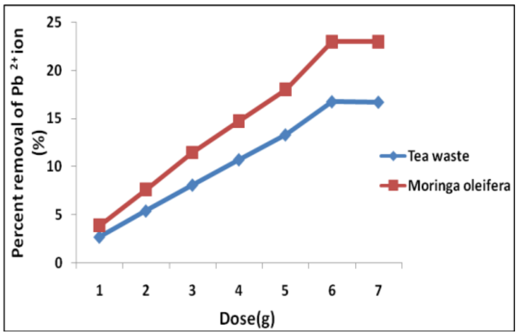


Figure 5. Effect of adsorbent dose on the removal efficiency for Pb^{2+} ion in aqueous solution by tea waste and char of *Moringa oleifera*

Effect of adsorbent dose

The amount of biosorbent dose were varied from 1 g to 7g and all other experimental variables such as pH, contact time, agitation speed, concentration of Pb^{2+} ions for tea waste and char of *Moringa oleifera* were kept constant. The experimental results are shown in Fig 5. There was an increase in biosorption capacity with increase dose from 1 to 6 g. This is because of the availability of more sorption sites also resulting from the increased dose of the biosorbent (Pehliven *et al*, 2009). The optimum removal efficiency for Pb^{2+} ions in aqueous solution by tea waste and char of *Moringa oleifera* were found to be 16.725 % and 22.98 % at 6 g of biosorbent.

Adsorption Isotherm

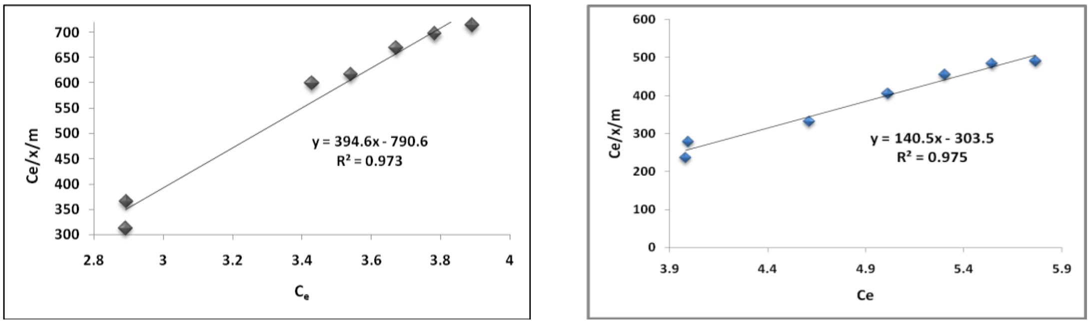
Langmuir and Freundlich isotherms are used in this experiment work. For solid-liquid systems the linear form of the Langmuir isotherm can be expressed by the equation (1)

$$\frac{C_e}{x/m} = \frac{1}{C_m b} + \frac{C_e}{C_m} \text{-----} \quad (1)$$

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

$$\text{Log}\, q_e = \text{Log}\,\frac{x}{m} = \frac{1}{n}\,\text{Log}C_e + \text{Log}\,K_f \text{ ---(2)}$$

Where, x/m or q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is equilibrium concentration of the adsorbate (mg L^{-1}), C_m (mg g^{-1}) gives the theoretical monolayer adsorption capacity ."b "(L mg^{-1}) is the Langmuir equation parameters and k and n are the Freundlich equation parameters.Langmuir isotherm for tea waste and char of *Moringa oleifera* is shown in Figures 5 (a) and (b).The Langmuir Isothermal parameters is shown in Table 2.The correlation coefficient 'R^2' values in Langmuir model was 0.973 for tea waste and 0.975 for char of *Moringa oleifera***.** The correlation coefficients of linearized Langmuir equation indicate that this model can explain an adsorption of metal ion by the materials satisfactorily (Karnitz *et al.*, 2006). The correlation coefficient 'R^2' values for tea waste and char of *Moringa oleifera* suggested that the adsorption data seen to be perfect positive relationship between the two variables. Monolayer adsorption capacity 'C_m' for char of *Moringa oleifera* **(**0.0071mg g^{-1}) was larger than the 'C_m' value of tea waste (0.0025mg g^{-1}). The essential features of the Langmuir Isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Weber and Chakravarti, 1974). The values of R_L indicate the nature of the isotherm, if the conditions are $R_L > 1$, $R_L = 1$, $0 < R_L < 1$ and $R_L = 0$ are unfavorable, linear, favorable and irreversible respectively. The value of R_L for removal of Pb^{2+} ions by tea waste and char of *Moringa oleifera* was 0.3307and 0.2642. These R_L values (less than one and greater than zero), showed that the two adsorption process were favorable. Freundlich adsorption isotherm was formed by plotting log x/m vs log C_e and the slope and intercept of this linear portion of Isotherm plots were determined by adopting graphical methodology. The Freundlich isotherm for Pb^{2+} ions is shown in Figure 6 (a) and (b). Table 3 shows the parameters of Freundlich Isotherm. The correlation coefficient 'R^2' values for tea waste and char of *Moringa oleifera* was 0.896 and 0.858. These values suggested that the adsorption data seen to good positive relationship between the two variables. The slope 1/n is a measure of adsorption intensity or adsorption process and the intercept values indicated an idea about adsorption capacity K_f. It was observed that the adsorption capacity of the char of *Moringa oleifera* for Pb^{2+} ions (K_f =5.1995×10^{-2}) was larger than the adsorption capacity of tea waste (K_f = 4.9317× 10^{-2}) .The constant K_f represents the quantity of Pb^{2+} ions adsorbed in mg g^{-1} adsorbent for a unit equilibrium concentration which is an approximate indicator of adsorption capacity. The 1/n value for removal of Pb^{2+} ions by tea waste and char of *Moringa oleifera* was 1.674 and 0.874 respectively. A variation in the slope (1/n) between 0 and 1 is associated with a chemisorptions process. On the other hand, 1/n being above one indicates cooperative adsorption (Freundlich, 1907).

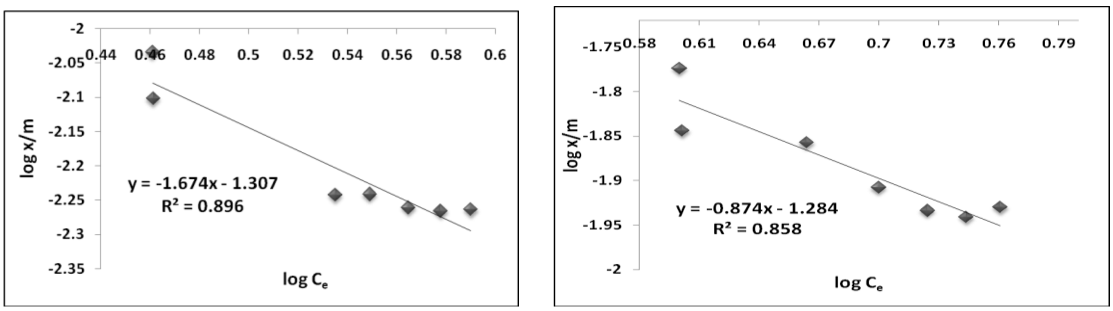


(a) **(b)**

Figure 6. (a)Langmuir isotherm for the tea waste and (b) char of *Moringa oleifera*

Table 2. Langmuir Parameters for the Tea Waste and Char of *Moringa oleifera*

Adsorbent	**Langmuir parameters**			
	C_m (mg g^{-1})	**b (L mg^{-1})**	**R^2**	**R_L**
Tea waste	**0.0025**	**0.5059**	**0.973**	**0.3307**
Char of *Moringa oleifera*	**0.0071**	**0.4640**	**0.975**	**0.2642**



(a) **(b)**

Figure 7. (a)Freundlich isotherm for the tea waste and (b)char of *Moringa oleifera*

Table 3. Freundlich Parameters for the Tea Waste and Char of *Moringa oleifera*

Adsorbent	Freundlich parameters		
	K_f	1/n	R^2
Tea waste	**4.9317× 10^{-2}**	**1.674**	**0.896**
Char of *Moringa oleifera*	**5.1995× 10^{-2}**	**0.874**	**0.858**

Removal of Pb^{2+} Ions by Tea Waste and Char of *Moringa oleifera* from Battery Repair

Business Waste Water

The removal of Pb^{2+} ions from battery repair business waste water using tea waste and char of *Moringa oleifera* by the batch method was carried out by the 6g of biosorbent, pH 4, contact time 40 min and agitation speed 100 rpm. The experimental result is as shown in Fig. 7. The initial Pb^{2+} ions concentration in battery waste water was 10 mg L^{-1}. The removal efficiency for Pb^{2+} ions by tea waste and char of *Moringa oleifera* were found to be 27.73 % and 33.65%.

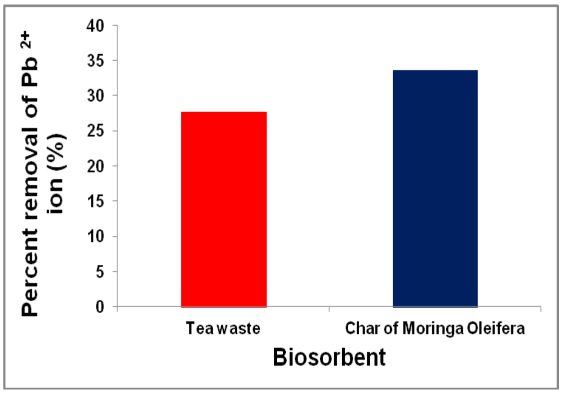


Figure 7. Removal of Pb^{2+} ions by tea waste and char of *Moringa oleifera* from battery repair business waste water

Conclusion

The adsorption of Pb^{2+} ions onto tea waste and char of Moringa *oleifera* depended on the initial Pb^{2+} ions concentration, pH, contact time, and adsorbent dose. Adsorption capacity decreased with increase in initial Pb^{2+} ions concentration but increased with increase in adsorbent dose and contact time. The percent removal efficiency for Pb^{2+} ions from aqueous solution by using tea waste was found to be 16.73 % at pH 4, 4mg L^{-1} initial Pb^{2+} ions concentration and 6 g of adsorbent dose. The percent removal efficiency for Pb^{2+} ions from aqueous solution by using char of Moringa *oleifera* was found to be 22.98 % at pH 4, 6 mg L^{-1} initial Pb^{2+} ions concentration and 6 g of adsorbent dose. The adsorption process was reaching equilibrium at 40min. The removal efficiency for Pb^{2+} ions from battery repair business waste water by tea waste and the char of *Moringa oleifera* at optimum condition of pH, contact time and dose were found to be 27.73 % and 33.65%.

Acknowledgements

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