

Fruit Stones as Adsorbents for the Removal of Lead Ion from Polluted Water

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ABSTRACT

Lead, one of the earliest metals recognized and used by humans, has a long history of beneficial use to humankind, but now been recognized as toxic and as posing a widespread threat to humans and wildlife. Treatment of lead from polluted water and wastewater has received a great deal of attention. Adsorption technique is one of the most technologies for the treatment of polluted water from lead, but seeking for the low-cost adsorbent is the target of this study. This study records experiments undertaken to determine the suitable conditions for the use of Peach and Apricot stones, produced from food industries as solid waste, as adsorbents for the removal of lead ion from aqueous solution containing this ion. Chemical stability of adsorbents, pH, adsorbents dose, adsorption time and equilibrium concentration were studied. The results reveal that adsorption of lead ions onto Peach stone was stronger than onto Apricot stone upto 4% at 5 hrs adsorption time. Suitable equilibrium time for the adsorption was 3-5 hrs (% Pb adsorption 95% for Apricot and 97.64% for Peach). The effective adsorption pH in the range 7-8. Application of Langmuir and Freundlich isotherm models show high adsorption maximum and binding energies for using these adsorbents for the removal of lead ions from contaminated water and wastewater.

Key Words

Adsorbents- wastewater- treatment- lead- pollution – solid wastes.

INTRODUCTION

Today, with the rapidly increasing urban population and water resources becoming more and more scarce, there is a strong need to reconsider our consumption patterns and the way we use our water resources. Developing countries suffers from water pollution; the high costs of contents and treatments make the major problems in these countries. Search for a cheaper alternative, reveals that utilizing natural processes and materials significantly reduce high cost. Natural adsorbents such as ores, rocks, plant straw and the dried aquatic plants are one of the effective and environmentally sound low cost materials for treatment of polluted water from heavy metals. The major point of water pollution was wastewater, especially urban wastewater, these urban wastewater come from varied sources include domestic wastewater from houses, hospitals and commercial uses as well as agricultural and industrial wastewater. This wastewater contains inorganic pollutants such as nutrient and heavy metals and causes pollution to the surface water .So, many studies were run to eliminate or reduce these pollutants before its discharge or reuse for irrigation. Wild and Stefist (1999) studied the simulation of nutrient fluxes in wastewater treatment plant with EBPR. Alum was used with ferric chloride as coagulators for the wastewater treatment (Ngtez et al, 1999). Many alkalis were currently being used for environmental control purposes particularly in wastewater treatments (Estefan, 1992); the most commonly used were lime and sodium carbonate.

Adsorption of the heavy metals ions from solution has been studied by others using naturally occurring minerals. Pyrolusite has been used for adsorption of Pb, Zn and Mg ions from their aqueous solution (Ajmal, 1995). Zeolites have been used for the removal of heavy metals from wastewater (Yuan et al, 1999). Sigworth and Smith (1972) and Muscas (1995) have also used adsorption techniques for the removal of heavy metals from polluted water. Other adsorbents that have been used for the removal of heavy metals solution include soils (Campbell and Davies, 1995) and carbonaceous material developed from fertilizer waste slurry (Srivestave et al, 1989). Adsorption of heavy metals ion from polluted water by activated carbons from date pits (Girgis and Hendawy, 1997) and by ferrite and chealating resin method (Tokunage and Uthium, 1997) have also been studied. Other workers such as Sigworth and Smith (1972) and Koshima and Onishi (1986) reported detailed investigations on the adsorption of metal ions on commercial activated carbons. Adsorption of arsenic at clay surface was studied (Lin and Pals, 2000). Mineral ores was used as adsorbents for the adsorption of ions from liquid phase (Dabrowshi and Tertyjh, 1992). Kaolinite and alumina were used for the removal of lead from incinerated lubricating oil by Hall (1998). Mn, Co, Ni, Zn and Pb were strongly adsorbed by the calcite surface in experiments by Reeder (1996). Coffee has been used for the removal of Pb, Cu, Hg, Cd and Zn from drinking water at a rate of 78-90 percent of the dissolved heavy metals (Strong, 2000).

Adsorption is a term commonly used for several different processes involving physical as well as chemical interactions between the solid surface of a substance and a dissolved metal species. Thus adsorption in general can be influenced by changes in hydrochemical parameters, such as pH and Eh.

The Langmuir equation was used as the model for adsorption by Bohn et al (1985), the adjusted Langmuir equation in its linear form being

$$1/(x/m) = 1/c b + 1/a$$

where a is Langmuir bonding energy coefficient.

b (mg/kg) is the adsorption maximum.

c (mg/dm) is the concentration of adsorbate left in solution at equilibrium.

x/m is the amount of adsorbate adsorbed per unit mass of adsorbent.

The Langmuir isotherm is constructed by plotting $1/(x/m)$ against $1/c$, if the data lie on a straight line then the Langmuir model can be considered to be appropriate. Using least square linear regression, the term b (reciprocal of the slope) and k ($1/b$) may be found.

Other model is the Freundlich isotherm, which is expressed as:

$$k/m = kc^{1/n}$$

Where x/m is the amount adsorbed per unit mass of adsorbent, c is the solution concentration at equilibrium, k and n are constants relating to adsorption capacity and intensity.

From this adsorption models; the adsorption maximum, binding energy, adsorption capacity and intensity can be calculated, and so the efficiency of the adsorbent for the removal lead can be obtained.

The aim of this study was to find out the effectiveness of new material with large surface areas that could be used as adsorbent for the removal of lead ions from polluted water.

EXPERIMENTAL

Sample collection

Synthetic polluted water samples

Synthetic polluted water samples containing definite concentration of Pb ion was prepared by diluting stock (1000ppm Pb) solution with bidistilled water .

Wastewater samples

The wastewater samples were taken from Kima drain (Kima drain, is a point discharge wastewater canal, come from fertilizer factory, sewage, hospital and house wastewater) This drain considered as one source of pollution input on River Nile water. Wastewater samples were collected by dipping pre-cleaned glass jars into the drain stream and collected in 20 L plastic container. Samples were placed in coolers and transported to the laboratory.

Adsorbent samples

Peach and Apricot stones were collected, washed with tap water then after by distilled water and allowed to dry in oven at 105°C for 5 hours. The dried samples were burned in a muffle furnace at 800°C for 2 hours and allowed to ground by using an electric agate mortar. The powdered sample was sieved in a sieve series <63 μm .

Standard Solutions

Certified atomic absorption spectroscopic standard solution as Pb (1000 ppm) was purchased from BDH Company , UK. Working standard solutions 5, 25, 100 and 500 ppm were prepared by diluting the stock one.

Analytical measurements

The polluted sample and the samples resulted from each treatment were analyzed for Pb using atomic absorption spectrophotometer, SP1900 Pye Unicam equipped with air-acetylene burner. Hollow cathode lamps of the studied metal were used at the recommended current and conditions.

Adsorption studies

Effect of Concentration

0.5 gm of each Peach and Apricot stones samples was treated with 50 ml lead standards (500, 100, 25, 5 ppm) in a conical flask for 24 h. After attainment of equilibrium, the content of the flask was filtered through Whatman 0.45 μ m cellulose nitrate membrane filter and Pb ion was analyzed using atomic absorption spectrophotometer. The final concentrations of Pb at equilibrium were determined, then the adsorption capacity was calculated.

Effect of pH on adsorption

One gram of each Peach and Apricot stones samples was treated with 50 ml of 25 ppm Pb standard, then the pH of the adsorption mixture was adjusted to various pH values (3, 5, 7 and 9) by using 0.5 M NaOH or 0.5 M HCl. The final concentration of the metal was determined after 24 h and the adsorption capacity was calculated.

Effect of ore dosage

0.25, 0.5, 1 and 2 gm of each Peach and Apricot stones samples was treated with 50 ml of 25 ppm Pb standard solution. The final concentration of the metals after 24 h were determined using AAS, and the adsorption capacity was calculated.

Removal of the lead ions from synthetic and polluted water

50 ml of the synthetic polluted water and/or wastewater sample was treated with 2 gm of each Peach and Apricot stones samples size <63 μ m in a conical flask; pH was adjusted to pH 7. After 5 hr shaking time the amount of metal concentration remaining was then determined by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Chemical stability of Peach and Apricot stones samples

The chemical stability of Peach and Apricot stones samples was determined in various solvents (distilled water, 1.0M NaCl, 0.1 M NH₄Cl, 1.0 M NH₄Cl, 0.1 M NaOH, 1.0 M NaOH, 0.01 M H₂SO₄, 0.01 M HNO₃, 0.01 M HCl and 0.1 M HCl). 0.5 g portions of kaolin sample was treated with 50 ml of the solvents for two weeks. After filtration, the studied heavy metals were determined in the filtrates.

Table 1: Effect of different solvents in Pb sorption of Peach and Apricot stones

Sample no.	Solvents	Pb concentration (ppm)	
		Peach	Apricot
1	distilled water	0.0	0.0
2	1.0M NaCl	0.01	0.0
3	0.1 M NaOH	0.0	0.0
4	1.0 M NaOH	0.0	0.0
5	0.01 M H ₂ SO ₄	0.03	0.045
6	0.01 M HNO ₃	0.12	0.22
7	0.01 M HCl	0.31	0.20
8	0.1 M HCl	0.25	0.65

Effect of initial metal concentrations.

From Table 2 ,it was shown that Pb undergo different adsorptions at adsorbent surface for all the initial lead standards. Parkman et al (1998) reported that per cent uptake of Sr on kaolinite was greatest at the highest initial Sr concentration.

Table 2 : Effect of initial lead concentration on adsorption efficiency

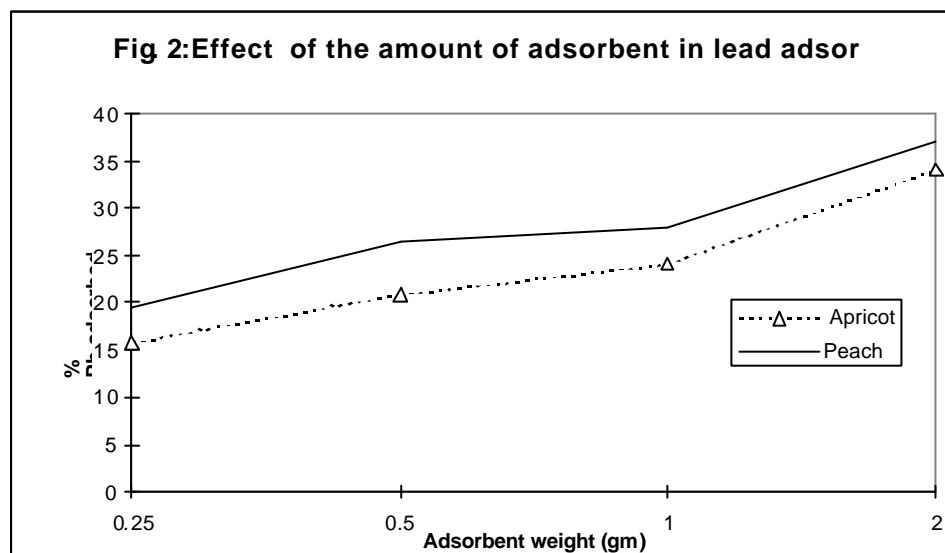
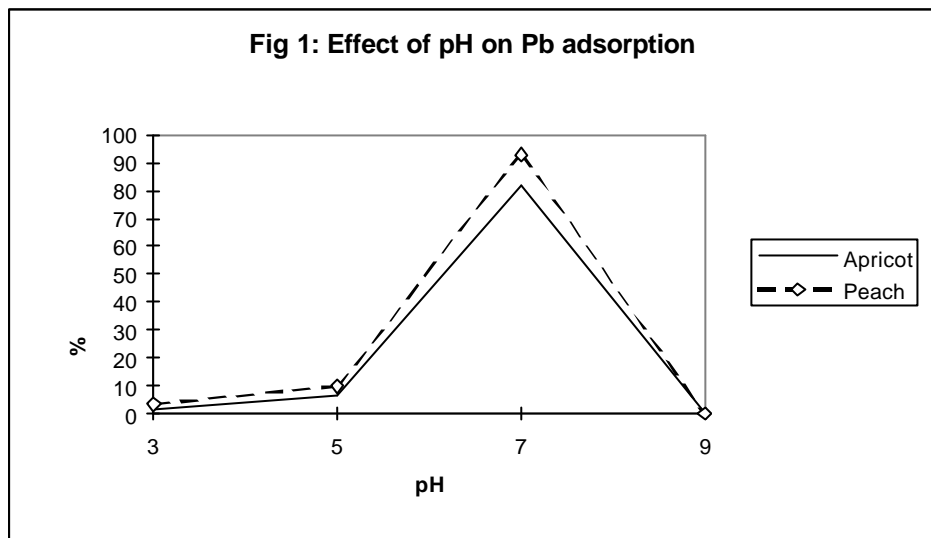
Element initial Concentration(ppm)	% Adsorption	
	Peach	Apricot
5	96	93.3
25	86	73.7
200	99.4	99.2
500	62.4	59.6

Effect of pH

The adsorption of lead on Peach and Apricot stones at different pH was performed using 25 ppm standard elements. The results (Fig.1) show that the adsorption of the studied lead increased as pH increase from 3 -6.5, the maximum adsorption of the metal observed at pH < 7. After pH 7 the metal adsorption decrease. Other study on the adsorption of heavy metals on the biomass of *Phormidium sp* was suitable at pH 5 for Pb, Cu, Cd, Zn and Ni (Wang et al, 1998), the maximum adsorption was 13,600 mg/kg for Pb; 10,100 mg/kg for Cu; 9,600 mg/kg for Cd ; 9,400 mg/kg for Zn and 5,700 mg/kg for Ni. Ajmal et al (1995) reported the maximum adsorption of Pb ,Zn and Cd on pyrolusite under pH 7. The optimum pH for removal of Cd, Cu and Mo using carbonaceous material, developed from the waste slurry generated from fertilizer plant, was about pH 6, for Cr and Hg was at pH 2, while for Pb it was almost in the range 6-7 (Srivestava et al, 1989).

Effect of Peach and Apricot stones dose

Using different dose of Peach and Apricot stones (0.5, 1, 1.5 and 2 gram) for the adsorption technique, suitable Peach and Apricot stones dose for the maximum adsorption of the studied lead was obtained (Fig.2). It shown that the adsorption of Pb increased as the adsorbent dose increase and reach maximum at 2g.



Effect of time on adsorption

From table 3 it can be seen that the adsorption of the studied lead ion on Peach and Apricot stones increased with time to reach its maximum adsorption at or after almost 5 hr . Koshima and Onishi (1986) reported an optimum time of contact 4 hr for the adsorption of heavy metals on commercial activated carbon.

Table 3: Effect of different times of lead adsorption on Peach and Apricot stones

Time Adsorbents	1 hr	3 hr	5 hr
Peach stone	93.64 %	97.64 %	96 %
Apricot stone	72.24 %	93 %	95.3 %

Langmuir adsorption isotherm

Langmuir equation was used as the model for adsorption, the adjusted Langmuir equation in its linear form being (Bohn et al, 1985)

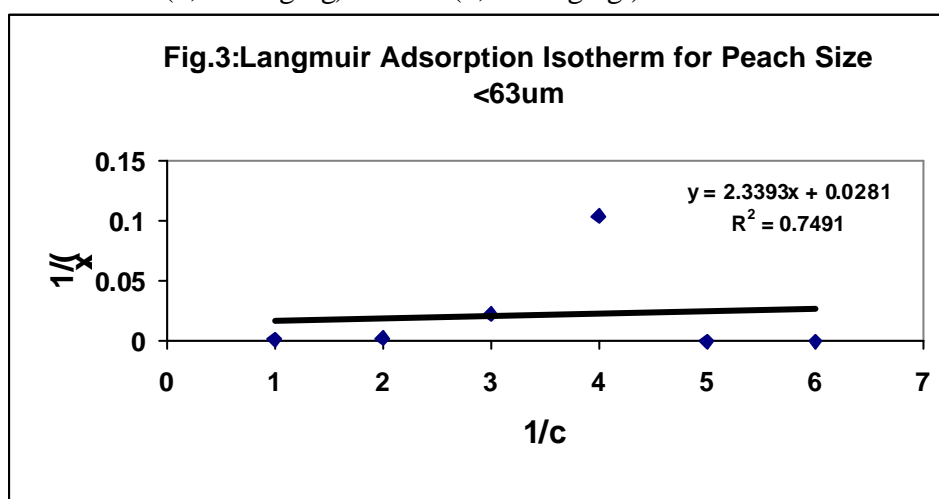
$$1/(x/m) = 1/c b + 1/a \quad (1)$$

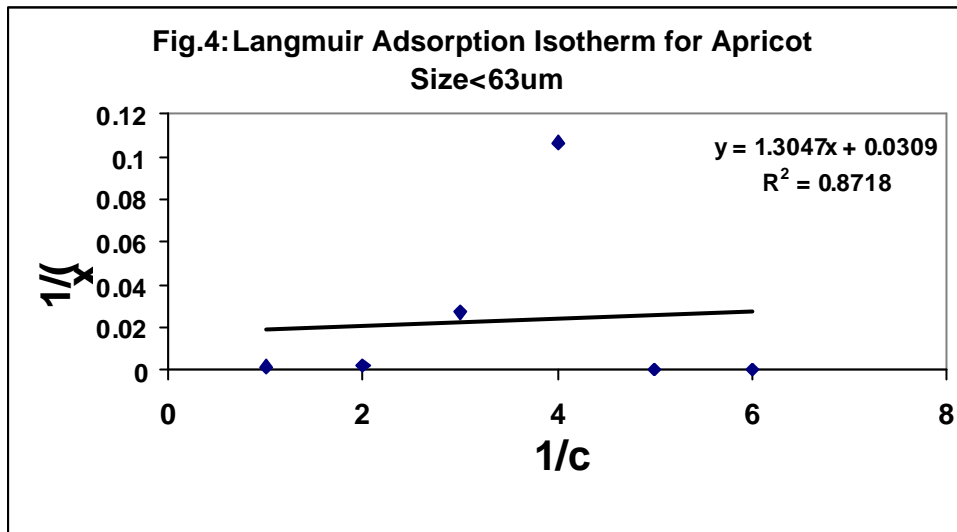
where c (mg/kg), is the concentration of adsorbate left in solution at equilibrium, x/m (mg/kg), is the amount of adsorbate adsorbed per unit mass of adsorbent, a , is Langmuir binding energy coefficient, and b (mg/kg), is the adsorption maximum.

Table 4 : Langmuir parameters for the adsorption of lead on Peach and Apricot stones

Adsorbent	Adsorption maximum a (mg/kg)	Binding energy B (mg/kg)	R^2 for Langmuir equation
Peach stone	2.33	0.028	0.749
Apricot stone	1.31	0.031	0.871

Parameters (a) and (b) can be obtained from equations in Fig. 3 and 4 and presented in Table 4. it was shown that the adsorption maximum of Peach stone is higher than of Apricot, while binding energy of Apricot is the highest. Correlation coefficient (R^2) obtained from Langmuir isotherms, were positive and highly significant. Other study (Wang et al, 1998) on the heavy metals binding and removal by *Phormidium sp* biomass reported the highly maximum adsorption, calculated from Langmuir isotherm, was for Pb (13,600 mg/kg) and Cu (10,100 mg/kg), while it was nearly the same for Cd (9,600 mg/kg) and Zn (9,400 mg/kg).





Freundlich adsorption isotherm

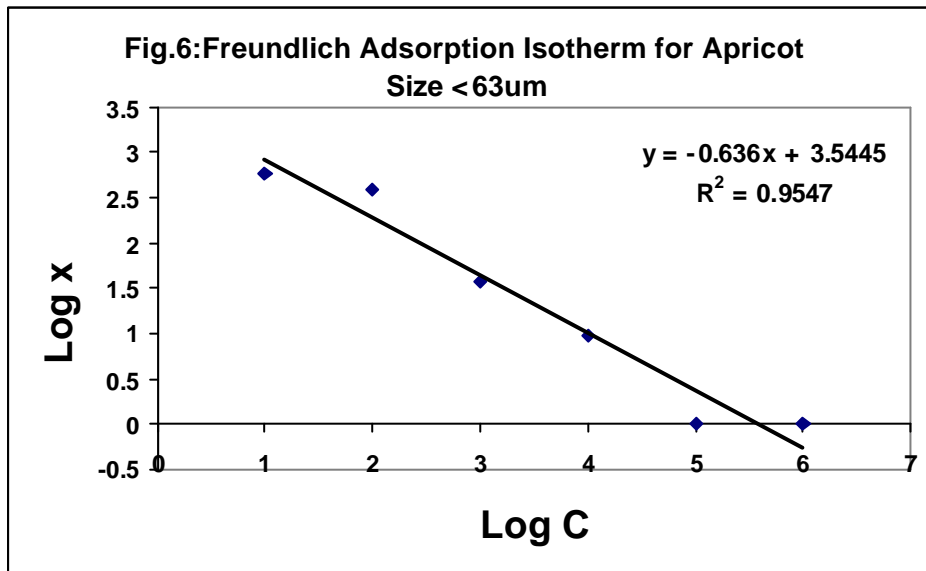
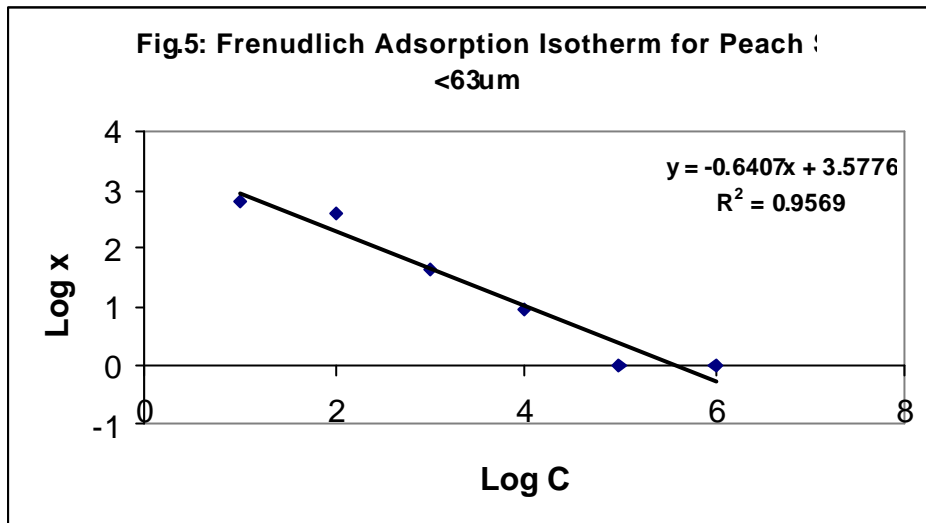
Applying Freundlich equation

$$k/m = kc^{1/n}$$

Where x/m is the amount adsorbed per unit mass of adsorbent, c is the solution concentration at equilibrium, k and n are constants relating to adsorption capacity and intensity. Freundlich parameters are obtained from Fig. 5 and 6. It shown from table 5 that the adsorption capacity of both Peach and Apricot are nearly the same.

Table 5: Freundlich parameters for the adsorption of lead on Peach and Apricot stones

Adsorbent	Adsorption capacity, k	Adsorption Intensity, n	R ² for Freundlich equation
Peach stone	0.640	3.57	0.956
Apricot stone	0.636	3.54	0.954



Wastewater treatment using Peach and Apricot stones.

After concluded the suitable conditions for the adsorption of lead ions on Peach and Apricot stones using synthetic standard solution, Kima drain wastewater was applied for the removal of Pb metal using Peach and Apricot stones. Treatment with Peach and Apricot stones exhibited the high efficiency for the removal of Pb from polluted water and wastewater

CONCLUSION

Peach and Apricot stones were very effective for removal Pb. The results of the wastewater treatment processes were in the limits cited by Egyptian Authority for discharge into surface water or reuse for irrigation.

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