*Removal of Pb(II) ions by adsorption from aqueous solutions using beans peel powder as a new adsorbent

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Abstract

In the present study, beans peel was used as an adsorbent for removing Pb(II) ions from aqueous solutions. The amounts of adsorbed ions were estimated were carried out by using flame atomic absorption spectrophotometer. The effects of initial metal ions concentration, pH, existing salt and temperature were studies.

The adsorption isotherms are of H-curve type according to Giles classification and the experimental data were best fitted to Langmuir and Freundlich isotherm models.

The adsorption phenomenon was examined as a function of temperature (20,30, 40 and 50°C) and various thermodynamic parameters (ΔH° , ΔS° and ΔG°) have been calculated. The thermodynamic parameters of lead ion- beans peel systems indicated the adsorption processes is spontaneous.

The results indicated that the adsorption extent of lead ions onto beans peel increased with increasing the pH of solution and it was decreased with increasing ionic strength of solution.

Introduction

Contamination of aquatic environment with heavy and toxic metals is a complex problem and their removal requires much attention . Their concentration gets accentuated through bioaccumulation via food chain in living tissues, causing various diseases and physiological disorders ⁽¹⁻³⁾. Hence the safe and effective disposal of contaminated water containing heavy metals like lead , Cadmium , Chromium , Mercury is always remained a challenge to the industrialists and environmentalists ⁽⁴⁾.

These heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders ⁽⁵⁾. All lead compounds are considered cumulative poisons. Acute lead poisoning can affect nervous system and gastrointestinal track⁽⁶⁾.

The attributable toxicity of lead to the fact that it and other heavy metals words for inhibitors effective interactions enzyme can also be interpreted toxicity of lead based on overlaps with groups of various enzymes as the (mostly) inhibits the work of those enzymes through its association totals (SH) in these enzymes proteins, or by sliding some of the major metal ions constituents such as calcium and on this basis, all member or regulations could be potential targets for attack of lead, leading to a wide dynamic effects, Lead is like most heavy metals are toxic ***The Research is apart of on MSC. Thesis in the case of the second researcher**

compounds and require large doses to some extent for toxicity but the risk increases because lead tends to cluster in the body (central nervous system) because of a property which is characterized by accumulation of lead as the rest of some heavy metals ions⁽⁷⁾.

A number of methods for the removal of heavy metals from aqueous solutions are available, including a reduction process, ferrous chloride treatment, biological treatment, biosorption and ion exchange followed by chelating resin⁽⁸⁾.

Adsorption technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents. Adsorption is widely used in the water and wastewater treatment industries, activated carbon remains an expensive material, the use of low-cost adsorbents is more suitable. A large number of low-cost adsorbents such as carrot residues ⁽⁹⁾, mango peel waste⁽¹⁰⁾, Powder of mosambi fruit ⁽¹¹⁾, waste of olive-oil production⁽¹²⁾, rice husk^(13,14), oil palm shell⁽¹⁵⁾, have been treated for heavy metals removal.

The aim of this work is to investigate the capability of peel beans for the removal lead ions from aqueous solution in different conditions of temperature, pH and ionic strength and to calculate the thermodynamic functions at equilibrium conditions.

Materials and Methods

Instruments:

1- Atomic Absorption Spectrophotometer, EA3000A, Euroea, Italy.

- 2- Shaker water bath, CL002, K&K Scientific, Korea.
- 3- Centrifuge, CL008, JANETZI T5, Belgium.
- 4- Electronic Balance, +0.0001g, Sartorius Lab. L420 B, Germany.
- 5- pH-Meter, BL 210S, Sartorius Ag Gottingen, Germany

Materials:

Hydrochloric acid ,sodium chloride and sodium hydroxide were supplied by Fluka and lead nitrate were supplied by BDH .

Preparation of The beans Peel

Grinding beans peel in the form of powder was washed with excessive amounts of distilled water; several washings were performed to remove dust and soluble materials. The powder was then dried under sunlight and then in an oven at 120° C for a period of 1.5 hour and kept in airtight containers.

Adsorption Isotherm

The adsorption isotherm were determined by shaking 0.2gm of surface into 10ml of metal ions solution, having concentration ranged between 50-500 ppm at pH 4.8. After 60 min. of shaking, the suspensions were centrifuged at 300rpm for 10 min. The metal ions concentration was determined spectrophotometer.

The quantity of metal adsorbed was calculated according to the following equation ⁽¹⁶⁾:-

Q	e Oľ	$\frac{x}{m} = \frac{V(C_o - C_e)}{m}$
	(1)	
Where :	Qe: sorption capacity (mg/g).	
	x : the quantity adsorbed (mg).	
	m : weight of adsorbent (g).	
	C _o : initial concentration (mg/L).	
	Ce : equilibrium concentration (mg/ L).	
	V : volume of solution (L).	

Effect of Temperature

Adsorption experiment was repeated in the same manner at different temperatures (20,30, 40 and 50°C) to estimate the basic thermodynamic functions of the process.

Effect of pH

Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of metals ions. Hydrochloric acid and sodium hydroxide were used to adjust the pH vale in the range from (1.0 to 6.8). The pH of the suspensions at the commencement of the adsorption was measured as well as at the end of experiment using pH-meter.

Effect of Ionic Strength

The effect of the addition (0.01-0.3g) of sodium chloride to solutions containing fixed concentration of metal ions equilibrated with 0.2g of beans peel were investigated under the same experimental conditions described before.

Results and Discussion

Adsorption and desorption Isotherm

Studied the time required to reach equilibrium concentration in adsorption lead ions on the surface of beans peel in different times was (0-180 min.) when the temperature (20° C) and constant concentration of ion (500 mg /L) and using that particle size of 150µm. Results of the study showed that the time required to reach equilibrium concentration is (30 mim).

The plot amount of adsorbent versus equilibrium concentration to give the general shape of Isotherm adsorption and desorption as shown in Figures (1), (2) respectively.



Figure (1): Isotherm lead ion adsorption on the surface of the beans peel at a temperature of 20°C



Figure (2) : Adesorption Isotherm lead on the surface of the beans peel at a temperature of 20°C

When comparing the curved isotherm adsorption obtained with isotherm curves adsorption shown in Figure (1), we find that they follow product (H) according to classification (Giles) as this kind achieved by the forces of different on different parts of the surface, as well less energy adsorption increase the covered part of the surface and adsorption increases with increasing concentration of material adsorbent ⁽¹⁶⁾.

These properties mean that the curve follows the equation (Langmuir adsorption) for the adsorption of : -

$$\frac{Ce}{Qe} = \frac{1}{q_m k_L} + \frac{1}{q_m}.Ce$$

.....(2)

Figure (3) show's the linear relationship of C_e/Q_e versus C_e . the values Langmuir

constants as well as the correlation coefficient are presented in table (1).



Figure (3) : Straight Langmuir lead ion adsorbed on the surface of the beans peel

Table (1): Langmuir constants for lead ions adsorbed on the surface of the beans peel

q_m	k_L	R ²
39.566	0.005	0.9943

Study the percentage of lead ion removal from aqueous solution at different times

The percentage of substance adsorbed on the surface of the beans peel used different times (0-120 min) was studied and recorded the amount of material removed of water aqueous as shown in Figure (4).



Figure (4): The percentage of lead ion removal from aqueous solution compared to the original focus at different times

The results showed that the percentage of lead ion removed from aqueous solution increases with time to end this surface saturation ions used as shown in Figure (4).

Effect of Temperature on Adsorption

The effect of temperature on the lead ion adsorption on the surface of the beans peel In different temperatures $(20, 30, 40 \text{ and } 50^{\circ}\text{C})$ was invistigated at acidic functions (4.8). It is through the use of equation (1) to calculate the amount of adsorbent.

The plot of amount of adsorbent (Q_e) versus equilibrium concentration (C_e) for the purpose of obtaining isotherm adsorption per degree temperature as shown in Figure (5), and indicate that the amount of adsorbent (Q_e) less with increasing temperature.



Figure (5): The amount of the adsorbent for lead ion on the surface of the beans peel at different temperatures

Thermodynamic functions of adsorption process were calculated and the results showed in a table (2) , which illustrates the adsorption process is "exothermic Process" as the temperature increases leading to increased kinetic energy of the molecules adsorbed on the surface adsorbent leading to disengagement lead ion surface . The results showed that the adsorption of the physical type where value of adsorption is ΔH lower (20 kJ.mol⁻¹).

 Table (2): Values thermodynamic equilibrium constant for the adsorption of lead ions on the beans peel

ΔH^{o} (kJ.mol ⁻¹)	$\Delta G^{o} (kJ.mol^{-1})$	$\Delta S^{o} (J.mol^{-1}.k^{-1})$	Equilibrium Constant
-5.441	-16.338	+37.193	731.2

Effect of pH

Several different acidic functions were used (0.1-6.8) to study the effect of pH on adsorption of lead ions on the surface of the beans peel at 20°C and

concentration (500 mg/L) . Through the use of equation (1) was extracted values (Q_e) were drawn against the acidic function as shown in Figure (6).



Figure (6) : The effect of pH at temperatures of 20°C and conce. (500 mg / L)

This can be explained by noting that the amount of adsorbent increases with increasing pH vale above 6.8 ions begin degradation, leading to the formation of hydroxides insoluble like pb (OH)₂.

Due to the fact that protons strong competing sorbate because of the higher concentration and high mobility and partly to the fact that the solution pH influences the sorbent surface charge .Any sorbent surface creates positive or negative charge on its surface. In acidic medium the adsorbent surface was highly protonated , which was not favorable for metal ion uptake. At higher pH values, the adsorbent surface began acquiring a net negative charge making the situation electrostatically favorable for a higher uptake of metal ion ⁽¹⁷⁾.

Effect of Ionic Strength

Several different concentrations of pure sodium chloride salt (0.01, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3gm) were used to study the effect of strength ionic adsorption of lead ions on the surface of the beans peel at 20°C at pH 4.8.



Figure (7): The effect of ionic strength at temperature of 20°C and pH (4.8)

This can be clarified by a competition between the sodium ions and lead ions in the adsorption on the surface of the beans peel including sodium ions characterized by a smaller size of lead ions. The transition ion in solution faster to the adsorption of sodium ions faster than the adsorption of lead ions.

Conclusions:

On the basis of the experimental results of this investigation, the following conclusions can be pointed out :

- 1- The results of atomic spectroscope show that the increase in the amount of adsorbent increase the time of equilibrium.
- 2- The beans Peel as adsorbent can be used for the removal Pb (II) ions from solution.
- **3-** Langmuir isotherm model adequately described the adsorption of Pb (II) ions onto beans Peel.
- 4- Thermodynamic studies confirmed that adsorption process of Pb (II) onto beans Peel was exothermic. The thermodynamic value of ΔG° is negative for system, indicating spontaneous process. As that type adsorption is physical from ΔH° through value ΔH interaction, which is equal to (-1.553 J.mol⁻¹).
- **5-** The percentage removal of metal ions was dependent on pH solution and ionic strength of sodium chloride solution.

<u>References:</u>

- 1- Wattoo. M.H.S., Iqbal J., Kazi .T.G and Jakhrani. M.A ., "Monitoring of pollution parameters in waste of tanneries in Kasur ", Pak .J .Biolog. Scis., <u>3</u>:960-962 (2000).
- Wattoo. M.H.S., wattoo. F.H., Tirmizi S.A., Kazi T.G., Bhanger M.I. and Ibex J., "pollution of Phulali canal water in the city premises of Hyderabad: Metal monitoring", J. Chem. Soc. Pak., :<u>28</u>:136-143(2006).
- 3- Sari. A., Tuzen. M., C1tak .D. and Soylak. M., "Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution", J. Hazardous Mater., <u>148</u>:387-394(2007).
- 4- Tewari. N., Vasudervan P.and Guha B.k., "Study on biosorption of Cr(III) by Mucor hiemalis", Bioche. Eng., J.,<u>23</u>:185-192(2005).
- 5- Bulut. Y. and Baysal. Z., J. of Environ. Manag., "Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste", <u>78</u>: 107-113 (2006).
- 6- Zhang .K., Cheung. W.H. and Valix. M., " adsorption of lead (II) and Cadmium(II) ions from aqueos solutions by adsorption on activated carbon prepared from cashew shells", Chemosphere., <u>60</u>: 1129-1140 (2005).
- 7- Thomas J.A., and Brogan W.C.," Some actions of lead on the male reproductive system", Am.J. Indus . <u>4 (4)</u> : 127 134(1983).
- 8- Anwar M. H., Deshkar A.M., Kelhar P.S., Dharmadhikari D.M., Hasan M.Z. and Paramasivam R.," Mercury Removal from Wastewater by Steamed Hoof Powder", Water Sci. Technol., 40: 109-116(1999).
- 9- Sadia A. Feroza H. W., Lala .R. S., Muhammad H.S. W. and Ahmed. T. Imran. D. "Biosorptive removal of lead and cadmium ions from aqueous solution: The use of carrot residues as low cost non-conventional adsorbent ", <u>37</u>: 272–279 (2012).
- 10- Bello O. S. and Ahmad M. A.," International Conference on Environmental Science and Technology., The history of indigenous agricul ture in soulution east asia-bibliogaphy", <u>v</u>₂: 103-106 (2011).
- 11- Hema. Krishnal R., and Swamy A.V.V.S.," Studies on Removal of Cr (VI) From Aqueous Solutions Using Powder of Mosambi Fruit Peelings (PMFP) As a Low Cost Sorbent", <u>9(3)</u> :1389-1399(2012).
- 12- Bulut Y. and Baysal Z., J.," Sequestration of toxic Pb(II) ions by chemically treated rubber (Hevea brasiliensis) leaf powderof Environmental Mangement", <u>78</u>: 107-113 (2006).
- **13-** Blazq G., Cakro M., Hernaiz F., Tenorio G. and Martin-Lara M. A.," Equilibrium biosorption of lead(II) from aqueous solutions by solid waste from olive-oil production Equilibrium Wastewater Treatment", Chemical Engineering J., <u>160</u>: 615-622 (2010).
- 14- Suemitsu.R., VenishiR., Akashi.I. and Nakano.M., "Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents Journal of Applied Polymer Science", <u>31</u>: 75-83 (1986).
- 15- Voyutsky S., "Colloid Chemistry", Mir publishers Moscow, p. 452 (1978).
- 16- Giles C.H., Macewan T.H., Nakhwa S.N. and Smith D.," A system of classification of solution adsorption isotherms, and its Use in Diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids", J. Chem. Soc., <u>786</u>: 3973-3993 (1960).
- 17-Hasan. S. H., Singh K., Prakash., Talat M. and Hoc Y. S., " Sorption equilibrium of mercury onto ground-up tree fern", J. Hazard Mater., <u>152</u>: 356-365 (2008).

*إزالة ايونات الرصاص بالامتزاز من المحاليل المائيه باستعمال مسحوق قشور الباقلاء كماده مازه جديده

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الخلاصة:

في هذه الدراسة استخدمت قشور الباقلاء كسطح ماز لإزالة ايونات الرصاص(II) من محاليلها المائية. وتم استخدام تقنية الامتصاص الذري اللهيبي لتقدير الكميات الممتزة ، كما درس تأثير تركيز الايون الفلزي ودرجة الحرارة والدالة الحامضية والقوة الايونية لمحلول الامتزاز . بينت الدراسة أن ايزوثيرمات امتزاز الايونين هي من نوع (H) طبقا لتصنيف Giles وان عملية الامتزاز نتبع ايزوثيرم لانكماير .

تم دراسة عملية امتزاز الايون الرصاص على سطح قشور الباقلاء عنده درجات حرارية مختلفة (ΔH°, ΔS°, ΔG⁰) ، كما حسبت الدوال الثرموديناميكية (ΔH°, ΔS°, ΔG⁰) لعملية الامتزاز وقد وجد أن عملية امتزاز ايون الرصاص على السطح تلقائية . أظهرت النتائج أن كمية ايون الرصاص الممتزة على هذا السطح تزداد مع زيادة الدالة الحامضية ونقصان القوة الايونية للمحلول.

*البحث مستل من رسالة ماجستير للباحث الثاني