Structural effects on the interactions of Pb(II) ion with Modified Banana Shell and Banana Shell during adsorption from aqueous solution

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ABSTRACT

Interaction of Pb(II) ion with modified banana shell (MBS) and banana shell (BS) during adsorption from aqueous solution were investigated. Batch experiments were carried out to investigate the effect of contact time, pH, and Pb(II) ion concentration on adsorption efficiency. The favorable pH for maximum Pb(II) adsorption was at 5.0. For the investigated Pb(II) concentrations (10–80 mg/L), maximum adsorption rates were achieved almost in the 100 min of contact. Langmuir, Freundlich, and Redlich–Peterson were fitted ta equilibrium data models. According to values of error functions and correlation coefficient, the Langmuir and Redlich–Peterson models were more appropriate to describe the adsorption of Pb(II) ions on MBS and BS. The monolayer maximum adsorption capacity of Pb(II) ions was determined as 104.2 and 45.3 mg/g for MBS and BS. respectively. Results indicated that these adsorbents had a great potential for removing of Pb(II) ions as an eco-friendly process

INTRODUCTION

Heavy metals contained in industrial effluents, constitute a major source of metal pollution of the environment, since they are persistent and cannot be degraded or destroyed and can be biomagnified by aquatic organisms. Main industries containing heavy metals in their effluents are mining, metallurgical, nuclear power plants, metal coating, and battery production [1].

Lead is the eighty-second element in the periodic table. Lead has a number of uses but many of these are currently being phased out because of growing awareness of its toxicity and of the damage that uncontrolled dispersion in the environment has already caused. Lead is employed in accumulators. ammunitions, piping, paints, in anti-radiation screens and tin-based welding alloys In the past. lead was added

to petrol in the form of tetraethyl lead $ph(C_2H_5)_4$ with an anti-knocking function: however, in developed countries this kind of petrol is currently being phased out for environmental reasons. Lead may also enter the environment as a by-product of mining and of the industrial processing of other metals, such as silver, gold, bismuth, etc.

Lead poisoning is a medical condition caused by increased levels of the metal lead in the blood. Lead may cause irreversible neurological damage as well as renal disease, cardiovascular effects, and reproductive toxicity [2]. Lead ranks second in the list of prioritised hazardous substances issued by the U S. ATSDR (Agency for Toxic Substances and Disease Registry) in

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1999. The noxious effects of this metal have long been well known, especially as regards acute forms of poisoning. However, as for many other contaminants, the threshold level of safety has been drastically lowered recently. Until approximately 30 years ago. chronic lead poisoning was defined by blood lead levels above 80 (gr/dl, while today a lead level of 30 (gr/dL in blood is considered excessive and levels at or above 10 (gr/dL (0.1 ppm) are considered potentially harmful, particularly in children [3].

Various methods of heavy metals removal from wastewaters have been the subject of different researches [4–7]. Most of these processes are unacceptable owing to their high cost, low efficiency. disposal of sludge, inapplicability to a wide range of pollutants. Adsorption, on the other hand. is one of the most recommended physico-chemical treatment processes that is commonly used and applied for heavy metals removal from water samples and aqueous solutions. In addition, adsorption process is well recognized as one of the most efficient methods for removal of heavy metals from their matrices Adsorption is mainly based on the utilization of solid adsorbents from organic, inorganic, biological or low cost materials [8, 9]. Heavy metal removal via adsorption by organic adsorbents is usually accomplished by the applications of polymeric ion-exchangers in which the binding and interaction of metal species with these adsorbents is favored via ion-exchange mechanism or by applications of chelating polymers whereas the target metal ions are directly attached to this kind of adsorbents via chelation or complex formation mechanism [10–13]. Naturally occurring materials either modified or unmodified. organic adsorbents such as chitosan and crosslinked carboxymethyl-chitosan, polysaccharide-based materials and lignocellulosic fibers with their surface characteristic functional groups in the form of hydroxyl or carboxyl were also found great research interests [14–16].

There is not much study on the removal of Pb(II) ions from water reported in the literature. Tarley and et al. [17] studied the adsorption of Pb(II) by modified rice husks as a natural solid adsorbent and Li and et al. studied the adsorption of Pb (II), Cr(III) and Cu(II) from aqueous solution by awdust and modified peanut husk [18].

Nabi and et al. used sawdust for adsorption of heavy metal ions from aqueous solution. They indicated increasing of capacity adsorption, followed sawdust modified with NaOH solution [19].

In this study, Pb(II) ion was selected as the target metal, since it is the one mainly found in wastewater due to its intensive use in industries. The objective of this study was the removal of Pb(II) ions from aqueous solution MBS and BS as a function of contact time, initial Pb(II) concentration, and pH regimes in a batch system. The adsorption capacity of this adsorbent was predicted by use of the equilibrium models. Furthermore, error functions were carried out to determine the best model.

EXPERIMENTAL

All the chemicals used in our experiments were of analytical grade. $Pb(NO_3)_2$ (molecular mass 331.20 g/mol CAS Number: 10099-74-8) were prepared from Merck Company with purity more than 99.99%. The BS preparation procedure was discussed in detail in a previous paper [20]. For preparation. MBS was immersed in NaOH (0.4 M) then HNO_3 (0.4 M) [20].

To evaluate the equilibrium properties, we first prepared various solutions with initial Pb(II) concentration ranging from 10 to 80 mg/L, and then added 3 g MBS and BS as adsorbent to each solution. These samples were then mounted on a shaker (HZQ-C) and shaken continuously for 10-120 min at 298 K. The suspensions were filtered using a 0.85 mm membrane. and the filtrates were immediately measured using atomic adsorption spectroscopy (AAS) (SHIMADZU model AA-6650). The differences between the initial and the equilibrium Pb(II) concentrations determine the amount that Pb(II) adsorbed by MBS and BS in separate solutions. The amount of Pb(II) ions per unit of adsorbent at time t (q_t; mg/g) and at equilibrium (q_{eq}. mg/g) were calculated by using Eq. (1) and Eq. (2), respectively:

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

$$q_{eq} = \frac{(C_0 - C_{eq})V}{m} \tag{2}$$

where C_n, C_t, and C_{eq} (mg/L) represent concentrations of Pb(II) at initial, at time, and at equilibrium in the solution, respectively V is the volume of solution (L), and m is the mass of the cach of adsorbents used (g)

In order to investigate the desorption capacity of Pb(II) from MBS and BS, 3g were introduced to 100 ml solution whose initial Pb(II) concentration is 50 mg/L and pH is 5.0. As the adsorption reaches equilibrium, the Pb(II) concentration of the solution was measured, and then the solution was filtrated using a membrane to recover the MBS and BS samples. These MBS and BS were dried at 60 °C and dispersed into 100 ml deionized water. The pH values of the solution were adjusted, from 2 to 6, using HCl and HNO_3 solutions, respectively. After the solutions reach equilibrium, the Pb(II) concentrations were re-measured and, the desorption results were then obtained.

RESULTS AND DISCUSSION
Effect of contact time and initial Pb(II) ions
In order to optimize contact time for adsorption, MBS and BS were prepared. Then the surfaces were treated by Pb(II) ion solutions with 50 mg/L af concentration, pH=5 and T=298K. The concentration of adsorbed ions on the surfaces was analyzed by AAS. The adsorption of Pb(II) ions on MBS and BS as a function of contact time and initial Pb(II) concentrations are shown in Figs. 1 and 2, respectively. The adsorption of Pb(II) ions (q_t, mg/g) increased with increasing contact time and initial Pb(II) concentrations by MBS and BS Rapid adsorption was observed during the first 80 min of contact time. It seems that 100 and 80 min is equilibrium contact time and with increasing of time, the amount of adsorption equilibrium is constant. Also 100 min is selected for contact time for MBS and BS adsorbents Similar results were also found in previous studies [21-24]. A change in the initial Pb(II) concentration from 10 to 80 mg/L caused an increase in the amount of adsorbed metal value from 4,965 to 39 799 mg/g and 8.222 to 65.876 mg/g for BS and MBS, respectively (Fig. 2). This could be due to an increase in the driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases. When the BS input NaOH (0.4 M) then HNO_3 (0.4 M) coordination bond formation

with –COOH group of MBS was postulated as the mechanism for the removal of Pb(II) ions [23, 24]. The reason for higher adsorption of Pb(II) ions by MBS is the existence of functional group (-COOH) on this adsorbent. This functional group causes a rise in the negative charge on the carbon surface. The oxygen atoms in the functional groups donate single pair of electrons to metal ions and consequently increase their cation exchange capacity [24]. It can be also related to the fact that carboxylic group on MBS can form a complex with the Pb(II) ions, leading to increase in the amount of ions adsorption [37, 38]. These results were also reported in previous studies [23, 25].
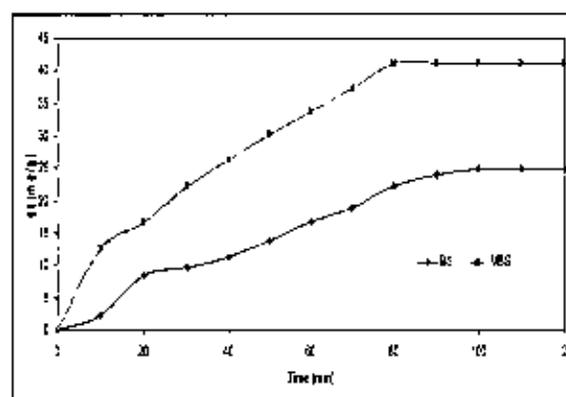

Fig. 1. Effect of contact time on the adsorption of Pb(II) ions by MBS and BS, initial Pb(II) 50 mg/L. pH=5 and T=298K.
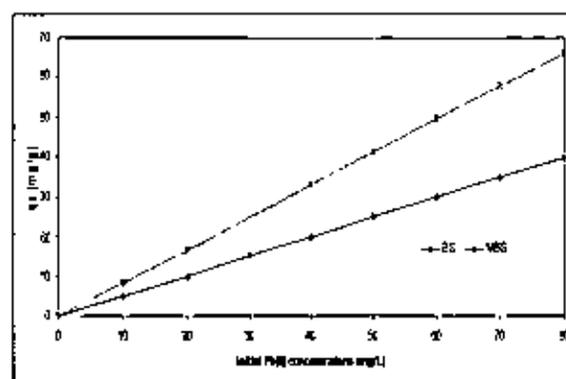

Fig 2. Effect of initial Pb(II) concentrations on the adsorption of Pb(II) ions by MBS and BS, contact time 100 min. pH=5 and T=298K.

Effect of initial pH regimes
The pH of the solution was one of the important factors governing the adsorption of Pb(II) ions. Initial pH regime has a critical role in metal adsorption by influencing the functional groups

nn the adsorbent surface and also the metal's snlubility. The pH range of solutions was adjusted to 2–6 because Pb(II) ions precipitated as Pb(OH)$_2$ in a solution with a pH value above 6 [25-27]. The effect of pH for the adsorption of Pb(II) ions on MBS aod BS are given in Fig. 3. The initial pH values strongly affected the adsorption of Pb(II) ions. At a pH, value of 2, the metal adsorption by the MBS and BS was found to be the lowest. At this pH. high concentration of H$^+$ ions could be very effective in excluding metal ions from binding to the sites on cell surface. Similar results were also reported in literature for the adsorption of some ions on different adsorbents [4, 5, 27].

The zero point charge (pH$_{zpc}$) of the adsorbent is one way to understand the adsorption mechanisms [11,13]. The pH$_{zpc}$ of MBS and BS were found as pH 8.1 and 7.2, respectively. where electrostatic repulsion between adsorbent molecules is at minimum. Whco pH of the solution is luwer than that of pH$_{zpc}$ values. the surface of the absorbent gets positively charged. This limits the adsorption capacity of metal ions due to electrostatic repulsioo. The amount of adsorbed metal at pH 2 was found to be lower than that at pH 5 because the surfaces of the absorbent get more positively charged at the lower pH [25-28]. Decreasing the pH of the solution causes to increase in positively charged (protons) group density oo the surface of the adsorbent, and electrostatic repulsion occurs between metal ions and functional groups on the surface. Therefore, adsorption capacity of adsorbents reduced with decreasing the pH of the solution [29].
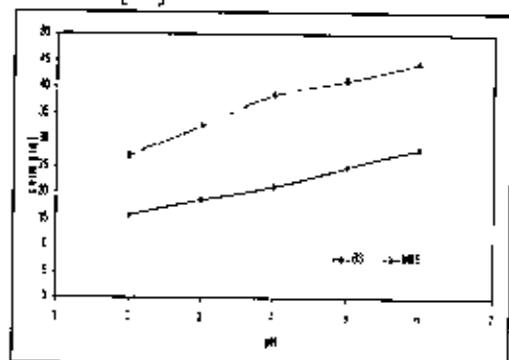

Fig. 3. Effect nf pH solution Pb(II) on the adsorption of Pb(II) ions by MBS and BS, initial Pb(II) concentrations, contact time 100 min, pH=5 and T=298K.

Adsorption isotherm

The relation of Pb(II) ion coñccotration in the bulk and the adsorbed amount at the interface is a measure of the position of equilibrium io the adsorption process and can generally be expressed by one or more of a series of isotherm models. The interpretation of adsorption data thrnugh theoretical or empirical equatinns is esseotial for the quantitative estimation of the adsorption capacity or amount of the adsorbent required lo remove the unit mass nf pollutant from wastewater. Fig. 4 and 5 shows adsorption isotherms of Pb(II) ion at 298K by BS and MBS, respectively In this study the experimeotal data were correlated by the non-lincar forms of Langmuir (Eq. 3). Freundlich (Eq. 4) and Dubinin-Radushkevich (D-R), (Eq. 5) adsorption isotherm equations

$$q_{eq} = \frac{Q^0 b C_e}{1 + b C_e} \tag{3}$$

$$q_{eq} = K_F C_e^{\frac{1}{n}} \tag{4}$$

$$q_{eq} = K_{D-R}(\varepsilon^2)^{-\beta} \tag{5}$$

where q$_e$ is the quantity of Pb(II) ion adsorbed at equilibrium over the mass of adsorbent material (mg/g) and C$_e$ is equilibrium conceotration (mg/L) of the adsorbate species in solution. Q^0 and b are Langmuir constants related to the monolayer adsorption capacity (mg/g) and eocrgy or intensity of adsorption (L/mg) The Freundlich constants K$_F$ aud 1/n are related to the adsorption capacity and heterogeneity factors related to binding strength, respectively. K$_{D-R}$ is D-R constant related to thcoretical saturation capacity and ε is the Polanyi potcntial, equal to RT ln(1+1/Cc), where R is the gas constant (kJ/mol K) and T is the temperature (K) [30-33]. Also. the Chi-square statistic (x^2) as error function is given by [34]:

$$x^2 = \sum_{i=1}^{m}\left[\frac{(q_{exp} - q_{cal})^2}{q_{cal}}\right] \tag{6}$$

where, q$_{exp}$ and q$_{eai}$ are experimental and calculated amount of adsnrhed Pb(II) per unit weight of adsorbent (mg/g). respectively.
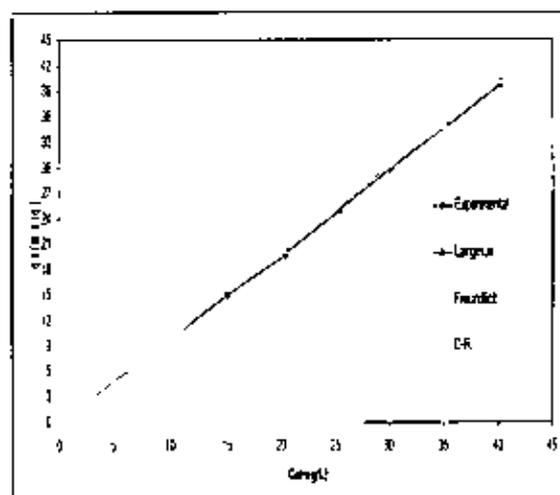
Fig. 4. Comparison of the experimental and model fits of the Langmuir, Freundlich and D-R isotherms for the adsorption of Pb(II) ions onto BS, contact time 100 min, pH=5 and T=298K.
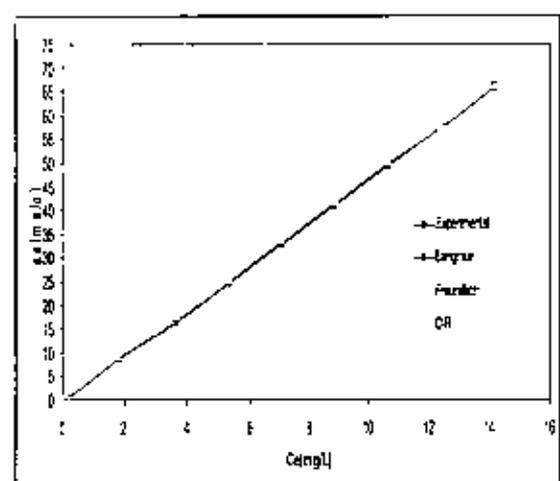

Fig. 5. Comparison of the experimental and model fits of the Langmuir, Freundlich and D-R isotherms for the adsorption of Pb(II) ions onto MBS, contact time 100 min, pH=5 and T=298K

A detailed analysis of the correlation coefficients obtained for these isotherms by using non-linear optimization method for Pb(II) adsorption, showed that all the two isotherm equations adequately describe the adsorption data, but are better fitted to Langmuir, from which we can assume that adsorption of Pb(II) ions onto BS and MBS would not take place beyond a monolayer coverage and all adsorption sites are equivalent with uniform energies of adsorption without any interaction between the adsorbed molecules. Figs. 4 and 5 also show a comparison between the theoretical Langmuir, Freundlich and D-R isotherms and the experimental data. The resulting parameters for all the three isotherms are tabulated in Table 1. As shown, Q^0 which is indicative of adsorption capacity changed in the order of MBS>BS. The Freundlich exponent 1/n gives an indication of the favorability of adsorption. Values of 1/n < 1.0 represent favorable adsorption condition. The values of 1/n obtained in the present study for Pb(II) ions are less than unity, which indicate the favorable adsorption of Pb(II) ions onto BS and MBS. The value of D-R constant β is related to the adsorption free energy E (kJ/mol), which is defined as the free energy change required transferring 1mol of ions from solution to the solid surface. From the β values the values of E can be calculated as $E = 1 / \sqrt{2\beta}$. The magnitude of E is useful to determine the type of adsorption reaction.

Physisorption processes have adsorption energy in the range 1–8 kJ/mol, while chemisorption processes have adsorption energy in the range 20–40 kJ/mol. On the other hand, adsorption can be explained by ion exchange if E values lie between 8.0 and 16.0 kJ/mol [35-37]. The calculated E values for Pb(II) adsorption onto BS and MBS are ranged 8.11 and 15.46 kJ/mol, respectively, indicating an ion exchange reaction, which support the idea, that the adsorption of Pb(II) ions onto BS and MBS mainly proceeds by binding surface functional groups, as stated earlier. The Langmuir parameters Q^0 and b are further used to predict the affinity between Pb(II) ions and adsorbent using the dimensionless separation factor $R_L = 1/(1+bC_e)$. The values of R_L indicate the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < RL < 1$) or irreversible ($R_L = 0$) [38]. The values of R_L for Pb(II) adsorption was determined over a wide concentration range at 298 K and the results confirmed the favorable uptake of Pb(II) ions onto BS and MBS. Also, higher R_L values at lower metal concentrations showed that adsorption was more favorable at lower concentrations [38-40].

Table 1. Isotherm parameters for the adsorption of Ph(II) ions onto BS and MBS

Isotherm parameters	BS	Pb(II)	MBS
Langmuir			
Q^0 (mg/g)	45.3		104.2
b(L/mg)	0.0016		0.088
R^2	0.9995		0.9996
X^2	0.12		0.11
Freundlich			
K_1	1.0059		3.081
1/n	0.9877		0.9408
R^2	0.9988		0.9990
X^2	11.12		10 08
D-R			
K_{D-R}	33.12		84.18
β	0 045		0 068
R^2	0.9981		0.9983
X^2	6.34		6.11
Ea (kJ/mol)	8.11		15.46

CONCLUSION

MBS is more effective than BS adsorbent for the removal of Pb(II) ions from aqueous solutions. Pb(II) removal increased with increase in pH and coordination bond formation with - COOH group nf MBS was postulated as the mechanism for the removal of Pb(II) ions. The amount of Pb(II) ions adsorbed per unit weight of MBS at equilibrium time increased with increase in concentration. The equilibrium data fitted better with the Langmuir isotherm equation compared to the Freundlich and D-R equations. The findings indicated that the maximum amounts of Pb(II) ions adsorbed on MBS and BS were found 104.2 and 45.3 mg/g, respectively.

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