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Removal of lead (II) and mercury (II) from aqueous solutions and waste water using pistachio soft shell as agricultural by-products

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Key words: pistachio shell; removal; heavy metal; agricultural by-product; Freundlich.

Abstract

In recent years, agricultural by-products have been widely regarded as metal removal from water. The object of this study is to investigate the possibility of using pistachio soft shell as low-cost effective alternative adsorbent for the removal of lead (II) and mercury (II) ions from aqueous solutions. Batch adsorption experiments were performed as a function of pH, temperature, contact time, initial metal ion concentration and adsorbent dose. Adsorption for both lead (II) and mercury (II) was found to be highly dependent on pH compared to the other parameters investigated. Obtained results gave a removal of 90.9(±2.8) % for lead (II) in the pH of 6, exposure time of 80 min at 25°C. Maximum removal of mercury (II) of 91.5(±2.1) % was obtained in pH 6 at 25°C after exposure time of 100 min.The Langmuir and Freundlich equations for describing sorption equilibrium were applied and the results indicate that the process was well described by Freundlich. Also adsorption kinetics data were modeled using the pseudo-first and pseudo-second order, it was found that the second-order model describes better the uptake of both ions. These results have demonstrated the immense potential of pistachio shell as an alternative adsorbent for toxic metal ions remediation in polluted water.

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Introduction

Monitoring the level of heavy metal ions in an aquatic ecosystem has received significant attention over many years because they are sever environmental pollutants and have adverse effects on human health(Lin *et al.*,2010). Serious consequences of biological hazards caused by metal toxicity cannot be ruled out (Das *et al.*, 2008). Lead and Mercury mediated toxicity has been widely reported to damage the brain, heart, kidney, gastrointestinal tract (Ercal *et al.*, 2001). There are many reported technologies for the recovery of metal ions from water and wastewater, such as chemical precipitation (Esalah *et al.*, 2000), flotation (Zouboulis *et al.*, 1997), electrolytic recovery, membrane separation(Canet *et al.*2002, activated carbon adsorption (Toles *et al.*,2002).

Biosorption is emerging as a potential alternative to the existing conventional technologies for the removal of metal ions from aqueous solutions. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery. Studies reveal that various by-products such as pine bark, banana pith, soybean, cotton seed hulls, peanut shell, hazelnut shell,rice husk, saw dust, wood, orange peel and eggshell have been widely has been used (Sud *et al.*, 2008; Park *et al.*,2007).

The dye (Blue 56) and zinc (II) ion are removed by raw pistachio shell from aqueous solutions (Tan *et al.*, 2007; Turan and Mesci 2011). Furthermore, carbon produced from pistachio shell has been investigated for Pb^{2+} ,Cd^{2+} , Zn^{2+} , Cu^{2+} and Hg^{2+} removal (Kazemipour *et al.*, 2008) .

In this study the removal of Pb^{2+} and Hg^{2+} from aqueous solution by raw pistachio shell was investigated. The adsorption capacity of adsorbent was examined by batch experiments .The effect of contact time, pH, temperature, metal ion concentration and amount of adsorbent studied and the obtained data were evaluated and fitted using adsorbent equilibrium isotherms and kinetic models.

Materials and methods

Reagents and equipment

All compounds used in the different tests are of analytical grade and were supplied by Merck. Doubly distilled water was used for preparation of all solutions. Atomic absorption spectrophotometer (AAS), model AA-240 Varian, US, was used for determination of lead and mercury contents. pH meter (Model Metrohm827) was used to check the pH of the metal solutions. For continuous shaking, Mechanical stirrer (Hieidolph, RZR2020) and for weighing electric balance of Sartorius (TE1245) were used.

Pistachio shell utilized for the current study was collected from Isfahan Province of Iran. The sorbent was grounded by electrical grinder, sieved (600-800 μm) and stored in contamination free atmosphere.

Metal Analysis

Stock solutions (1000 mg/L) of Hg(II) and Pb(II) ions were prepared from $HgCl_2$ and $Pb(NO_3)_2$. All experimental solutions (2 to 40 mg/L) were prepared by diluting the stock solution to the required concentration.

The lead contents were measured by using atomic absorption spectrophotometer at 217.0 nm. and mercury at 253.7 nm. The instrument was calibrated within the linear ranges of analysis and correlation coefficients of 0.998 for lead and 0.995 for mercury were obtained based on calibration curves. The amount of adsorption onto the biomass was assumed to be the difference between the initial metal concentration and concentration that found in the supernatant. The lead and mercury uptake was calculated by the simple concentration difference method (Volesky and Holan, 1995).

Batch Adsorption Experiments

Batch adsorption experiments were conducted at optimum temperature. For each experimental run, 100 mL of metal solution of known initial concentration were taken in a reagent bottle. A suitable adsorbent dose was added to the solution and the mixture was shaken at a constant agitation speed. Samples were withdrawn after optimum time and then filtered. The filtrate was analyzed for residual metal concentration. The effects of pH, contact time, temperature, initial concentration and dose of adsorbent were investigated.

Data quality assurance

The validity of models was determined by calculation the standard deviation (S.D., %) using Eq. (1)

$$S.D.\% = \sqrt{\frac{\sum[(q_{exp}-q_{cal})/q_{exp}]^2}{n-1}} \times 100 \quad (1)$$

Where the subscripts exp and cal refer to the experimental and the calculation data, and n is the number of data points (WU, 2007).

Results and discussion

The effect of pH on adsorption of metal ions

To investigate the role of pH in removal efficiency of Hg(II) and Pb(II), the initial pH of the adsorbate solutions was varied in the range of 2–8. The adsorption capacities were found to be low at low pH values and increased with increase in pH. This can be explained with competitive adsorption of H_3O^+ ions and metal ions for the same active adsorption site.

The adsorption study could not be carried out experimentally at pH values higher than 8 due to the precipitation of Pb hydroxide in this pH range.

It can be seen that the removal percent of both Hg (II) and Pb(II) are maximum, 94.0% and 95.0% respectively, at pH 6.

The effect of temperature

For evaluation the effect of temperature on removal efficiency experiments were performed at different temperatures 20, 40, 60, 80, 100 and 120 °C at a concentration of 10 mg $L^{-1}$and pH of 6.0. The uptake increased with rising temperature from 58.2% to 75.4% for lead and from 48.6% to 82.2% for mercury (Fig. 2).

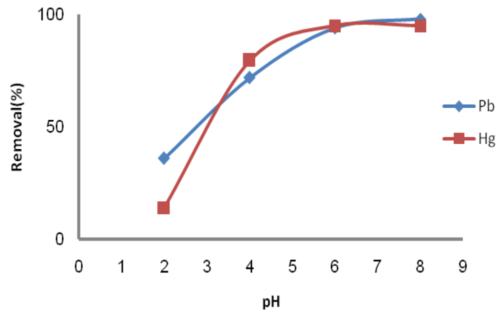

Fig. 1. Effect of pH on the adsorption heavy metal ion onto pistachio shell.

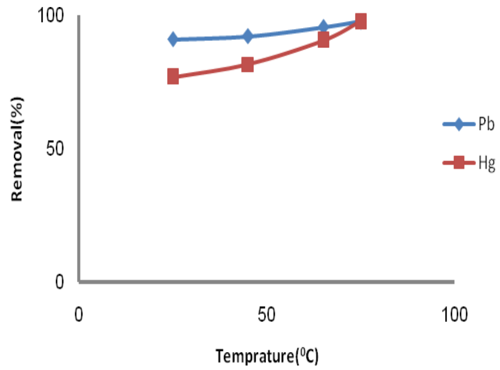

Fig. 2. Effect of temperature on the adsorption heavy metal ion onto pistachio shell.

The effect of concentration of metal ion

As seen in Fig. 3, at high concentrations the responsible sites for metal uptake are saturated. The results obtained in this section can be used for drawing the Langmuir and Frundlich adsorption isotherm. Langmuir curve calculates the maximum adsorption theoretically.

The effect of agitation time

The effect of agitation time was studied for two metal ions. Fig. 4 shows that the removal increases sharply with increasing agitation time up to 40 min and then it increases very slowly and becomes nearly constant after 50 min. It means that thermodynamic equilibrium is attained at that time.

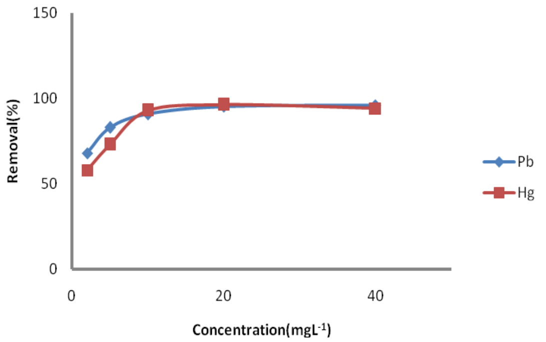

Fig. 3. Effect of initial concentration on the adsorption heavy metal ion onto pistachio shell.

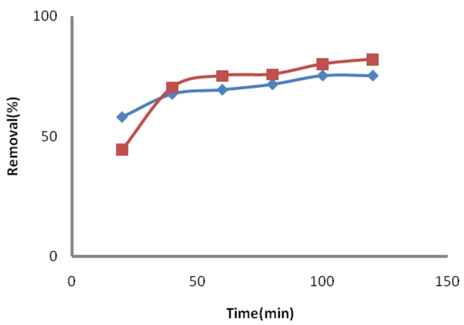

Fig. 4. Effect of contact time on the adsorption heavy metal ion onto pistachio shell.

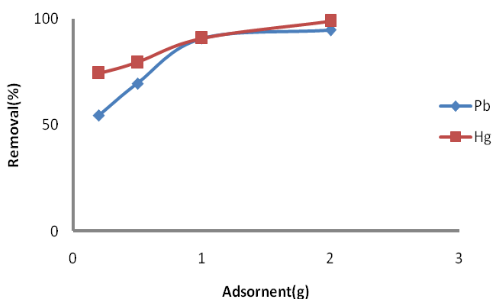

Fig. 5. Effect of adsorbent dosage on the adsorption heavy metal ion onto pistachio shell.

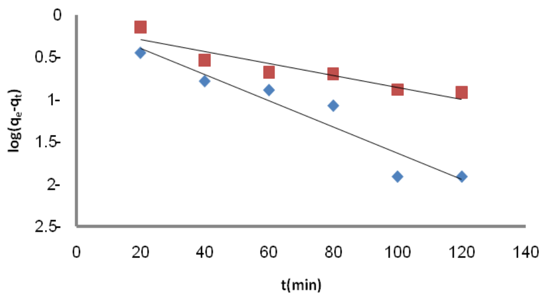

Fig. 6. pseudo-first-order plot of adsorption heavy metal ion onto pistachio shell.

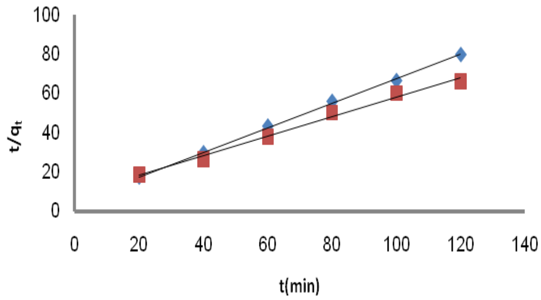

Fig. 7. pseudo-second-orderplot of adsorption heavy metal ion onto pistachio shell.

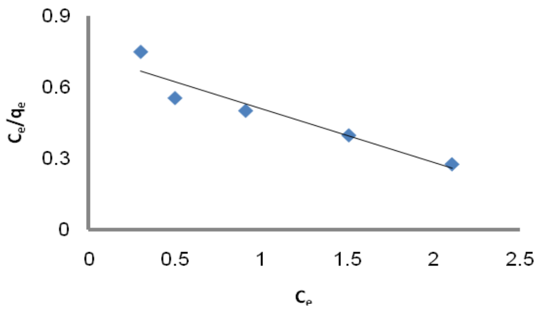

Fig. 8. Langmuir isotherm plot of adsorption lead ion onto pistachio shell.

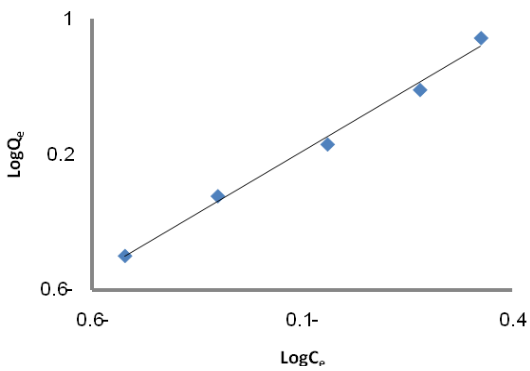

Fig. 9. Freundlich isotherm plot of adsorption lead ion onto pistachio shell.

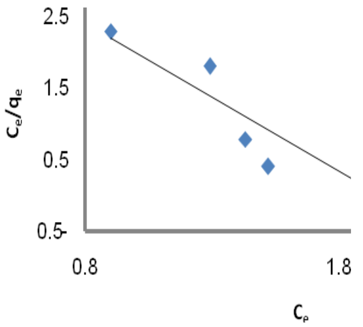

Fig. 10. Langmuir isotherm plot of adsorption mercury ion onto pistachio shell.

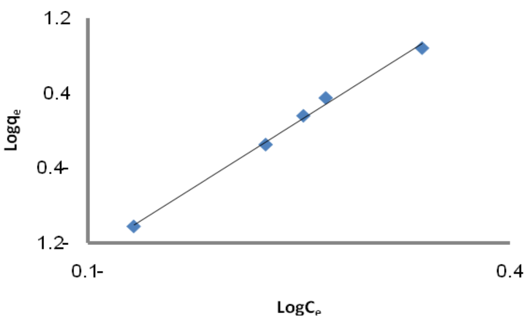

Fig. 11. Freundlich isotherm plot of adsorption mercury ion onto pistachio shell.

The effect of adsorbent dose

The dependence of metal ions removal on adsorbent dose was investigated by varying the amount of Pistachio shell from 2 to 20 g/l, while keeping other parameters constant. It is clear from fig. 5 that the amount of removal increases by increasing adsorbent dose. This can be explained based on the fact that the higher the adsorbent dose in the adsorbate solution, the greater the availability of exchangeable sites for metal ions.

Adsorption Kinetics

The kinetic data obtained were analyzed using pseudo-first- order rate and pseudo-second-order rate respectively Eqs. (2 and 3).

$$\log(q_e-q_t)= \log q_e- k_1t /2.303 \quad (2)$$

$$t/q_t=1/k_2q_e^2+t/q_e \quad (3)$$

where qe and qt (mg g-1)are the amount of metal ions adsorbed on the sorbent at the equilibrium and at time (min), respectively. k_1 (min−1) and k_2 (g mg−1 min−1) are the rate constant of adsorption (WU, 2007).

In order to investigate the adsorption kinetics of Pb(II) and Hg(II) metal ions onto pistachio shell and to evaluate the goodness of the fit of experimental data the pseudo-first-order and pseudo-second-order model and a normalized standard deviation SD(%) were calculate.

The adsorption kinetic constant and linear regression and S.D. % value are summarized in table 1.

Table 1. Kinetic parameters of the pseudo-first-order and pseudo-second-order models.

Ion Metals	pseudo-first-order			pseudo-second-order		
	K_1	R^2	SD%	k_2	R^2	SD%
Hg	0.0143	0.872	7.81	0.0016	0.991	3.78
Pb	0.0173	0.910	6.32	0.0024	0.999	2.87

The estimated model and related statistic parameters are reported. Based on linear regression (R^2>0.99) values , the kinetics of lead and mercury adsorption on to the pistachio shell can be described well by pseudo-second-order equation .The value of S.D. % for the pseudo-second-order is lower than that for the pseudo-fist-order kinetics model.

Adsorption isotherms

The adsorption isotherm indicates how the adsorbate ions distribute between the liquid phase and the solid phase at equilibrium. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model for describing the adsorption mechanism.

In this research, adsorption isotherm study was carried out on two well known isotherms, i.e., Langmuir and Freundlich. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface and represented as follows Eqs. (4):

$$C_e/q_e = C_e/q_m + 1/q_m K_L \qquad (4)$$

Where q_m (mg g−1) is the monolayer adsorption saturation capacity, and K_L (Lmg−1) Langmuir constant related to adsorption energy. Fig. 3 shows the Langmuir plots for two metal ions and the constants q_m and K_L are tabulated in Table 2. High R^2 values (>0.98, Table 2) indicate that the biosorption of Pb(II) and Hg(II) onto pistachio shell follows the Langmuir model. The Freundlich isotherm is suitable for a highly heterogeneous surface and expressed by the following Eqs. (5):

$$\log q_e = \log C_e/n + \log K_F \qquad (5)$$

where K_F ($mg^{(1-1/n)}$ g−1 $L^{1/n}$) and 1/n are the Freundlich constants, they denote the adsorption capacity and intensity, respectively.

The estimated model parameters with correlation coefficient and the S.D.% values for two models are shown in table 2.

Table 2. Coefficient of Langmuir and Freunlich isotherms.

Ion Metals	Langmuier				Freundlich			
	q_{max}	K_l	R^2	SD%	K_F	n	R^2	SD%
Hg	4.184	0.343	0.982	13.94	6.486	0.551	0.997	3.553
Pb	2.299	0.573	0.978	15.97	19.76	0.512	0.992	5.97

Based on the modeling, the Freundlich isotherm describes better the adsorption of Pb(II) and Hg(II) metal ions onto pistachio shell rather than the Langmuier isotherm. The applicability of the two isotherm models for the present data follows this order: Freundlich>Langmuiercase of lead and mercury ions.

Table 3. Recovery percentage of pistachio shell in removing Pb(II) and Hg(II) for synthetic and real samples.

	Recovery%	
	Pb(II)	Hg(II)
Synthetic sample 1	93.2	98.2
Synthetic sample 2	91.4	99.1
Real sample 1	87.5	91.6
Real sample 2	88.4	92.4

Real sample analysis

Optimum conditions used for various metal ions on pistachio shell in synthetic and real (wastewater) samples. Results have been shown in table 3.

These results indicate that about 90% of the heavy metal ions removed from the wastewater.

Conclusions

The results of present study show that pistachio shell has considerable potential for heavy metal ions removal from aqueous solution over a wide range of concentration Adsorption on pistachio shell can be expressed better with Freundlich type adsorption isotherms which shows the heterogeneous characteristics of the adsorption sites on pistachio shell. Adsorption capacity order was found as Pb(II) >Hg(II).

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