RESEARCH ARTICLE
• Arch Hyg Sci 2017;6(1): 32-38
• Journal Homepage: http://jhygiene.muq.ac.ir

Optimization of Continuous Flow Adsorption of Heavy Metal Ions by Peganum Harmala Seeds

Elhameh Mohammadpour[a], Mohammad Reza Yaftian[a], Abbasali Zamani[b] Parvin Gharbani [c,*]

[a]Phase Equilibria Research Lab., Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran.
[b]Envirnmental Science Research Lab., Department of Environmental Science, School of Science, University of Zanjan, Zanjan, Iran.
[c]Department of Chemistry, Ahar Branch, Islamic Azad University, Ahar, Iran.

***Correspondence** should be addressed to Dr. Parvin Gharbani, **Email:** p-gharbani@iau-ahar.ac.ir, parvingharbani@yahoo.com

A-R-T-I-C-L-EI-N-F-O

Article Notes:
Received: Jul. 1, 2016
Received in revised form: Nov. 11, 2016
Accepted: Nov. 21, 2016
Available Online: Jan 1, 2017

Keywords:
Peganum harmala seeds
Adsorbent
Adsorption
Continuous Flow
Heavy Metals
Iran.

A-B-S-T-R-A-C-T

Background & Aims of the Study: Heavy metals discharge to environment is a worldwide problem growing in scale. When they accumulate in the environment and in food chains, they can profoundly disrupt biological processes. Peganum Harmala Seeds (PHS) was used as a bio-sorbent, using a continuous system for removing Pb^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions from aqueous solutions.

Materials and Methods: PHS was used as adsorbent in adsorption of heavy metals from aqueous solutions. A stock solution of Pb(II), Co(II), Cu (II) and Ni (II) was prepared and experiments were down in a column as a reactor. The concentration was determined by atomic adsorption spectroscopy. The effect of various parameters such as pH, contact time, heavy metal concentration, ionic strength, particle size and adsorbent dosage on the process was investigated. Langmuir, Frundlich and Temkin isotherms were studied to evaluate of adsorption isotherms.

Results: The adsorption efficiency was found to be pH dependent and enhanced by increasing the solution pH. Maximum removal of ions were obtained at pH=4-8. The equilibrium time was attained after 30 min and desorption studies were performed, using diluted HNO_3, H_2SO_4 and HCl solution (1M) on adsorbed metal ions from PHS. Results illustrated that adsorbed metal ions could be recovered under acidic conditions. Investigation of the process kinetic was best fitted with pseudo second-order model. Langmuir, Freundlich and Temkin models were tested for describing the equilibrium data. The Langmuir isotherm illustrated the best description of the cobalt and copper adsorption mechanism and Freundlich model describes lead and nickel ions adsorption on PHS.

Conclusion: It was found that PHS would be a good adsorbent for removal of heavy metals.

Please cite this article as: Mohammadpour E, Zamani A, Yaftian MR, Gharbani P. Optimization of Continuous Flow Adsorption of Heavy Metal Ions by Peganum Harmala Seeds. Arch Hyg Sci 2017;6(1):32-38.

Background

The production of waste with high heavy metal ions content is a serious problem due to the disposal of heavy metals. Heavy metals discharge into water by industries such as mining, metallurgy, electronics, textiles, oil refineries and pulp (1-3). These metals increase health risks in animals, plants and human (4). Examples of heavy metals are (Cd), (Hg), (Pb), (Cu), (Cr), (Ni), (Zn), (As), (Co), (Ag), (Au), (Se), (V), (Sb), (Bi), (Mn), (Ce), (Ga), (Pt), and (Fe) that may be caused to many diseases such as central nervous system irritation, depression, affect the skin, lungs etc (5). There is a permissible limit of heavy metals in water. For example, guideline values for Cu, Ni, Pb and

Cd are 2, 0.07, 0.01 and 0.003 mg/L, respectively (6,7). In order to remove these metals different methods are examined, such as chemical and electrochemical precipitation, coagulation and electrochemical deposition, ion exchange resins etc. These methods do not seem to be economical in large scales (8). So, it is necessary to investigate a low-cost method which is effective and economic. Adsorption is a simple process. It is high efficiency, easy and cost-effectiveness (5). There are a lot of cheap adsorbents for removal of containments from waters such as agricultural waste (9-10), powder of leaves and branches (11), rice bran (12), sawdust (13), peels (14), green algae (15), and so on(16). Adsorption capacity depends on the nature of adsorbent, their porosity and large surface area with more specific adsorption sites. There are three types of adsorption: chemical, physical and electrostatic. The popular adsorption is physical type (17).

Aims of the study:

The aim of this research is to study the efficiency of PHS as low-cost adsorbent in the removal of Cu, Ni, Pb and Cd ions from aqueous solutions. The effects of some key parameters on adsorption such as contact time, pH, initial concentration, adsorbent size and ionic strength were studied.

Materials & Methods

This research is an experimental research that was carried out in Environmental Science Research Lab. of Zanjan University.

Preperation of Adsorbent

Peganum Harmala Seeds (PHS) were purchased from Zanjan, Iran. They were washed three times by drinking water and then by distilled water. Then they were dried in an oven for 24 h in 70 °C. The dried PHS was used as an adsorbent in adsorption of heavy metals from water.

Adsorption experiments

Adsorption experiments were performed by a continuous method. A stock solution of Pb(II), Co(II), Cu (II) and Ni (II) was prepared by dissolving $Pb(NO_3)_2$, $Co(NO_3)_3$, $Ni(NO_3)$, $Cu(NO_3)_2$ in a distilled water. Experiments were down in a column (15*3 cm) as a reactor. Samples were collected from the end of the column at different time. Samples were separated by centrifugation at 4000 rpm for 10 min. The concentration was determined by an atomic adsorption spectroscopy. The initial pH of the solution was adjustment either NaOH or HCl in the range of 1-8. Samples were taken each 5 minutes and analyzed by an atomic absorption spectroscopy. The amount of adsorbed heavy metals on adsorbent (q, mg/g), adsorption percent (%A) and desorption percent were calculated, using general equation (1), (2) and (3).

$$q_e = \frac{(C_0 - C_t)V}{W} \qquad (1)$$

$$\%Adsorption = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (2)$$

$$Desorption = \frac{m_d}{m_a} \times 100 \qquad (3)$$

Here, q_e is the adsorption amount (mg/g), C_0 and C_t are the initial and final concentrations (mg/L), V the volume of solution (L), W is the mass of adsorbent (g), md desorbed heavy metals (mg) and ma adsorbed heavy metals (mg).

Analysis

The concentrations of heavy metals were determined by a flame atomic absorption spectrometer (Shimadzu, Japan). The pH of solution was measured by a pH meter (Metrohm 620 pH lab). The functional groups on the surface site of Peganum Harmala Seeds were characterized, using a Fourier transform infrared spectroscometer (FT-IR Nicolet is 10/Thermo) in the range of 500-4000 cm^{-1}.The surface morphology of Peganum Harmala Seeds was taken by scanning electronic microscopy (Mira tescan).

Adsorption isotherms and kinetics

The adsorption isotherms for the Pb(II), Co(II), Cu (II) and Ni (II) removal were studied, using various initial concentrations. Equilibrium adsorption isotherm data were analyzed according to the linear forms of Langmuir, Freundlich and Temkin adsorption isotherm equations (4-6), respectively:

$$\frac{1}{q_e} = (\frac{1}{K_L q_m})\frac{1}{C_e} + \frac{1}{q_m} \qquad (4)$$

$$Lnq_e = (\frac{1}{n})LnC_e + LnK_F \qquad (5)$$

$$q_e = B_1 LnC_e + B_1 LnK_T \qquad (6)$$

Where q_m is the maximum adsorption (mg/g) and K_L is the Langmuir constant including the affinity of binding sites (L/mg). K_F and n are the Freundlich constants indicating adsorption capacity ((mg/g) (L/mg)1/n) and intensity, respectively. K_T and B_1 are the Temkin constants. K_T is the equilibrium binding constant (L/g) and B_1 is related to the heat of adsorption.

For studying the kinetic sorption, pseudo-first order (7), pseudo-second order (8), Elovich (9), and power function (10), models were studied (18).

$$Ln(q_e - q_t) = -k_1 t + Lnq_e \qquad (7)$$

$$\ln q = \ln k + v \ln t \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

$$q_t = \frac{\ln a_E \beta_E}{\beta_E} + \frac{1}{\beta_E} \ln t \qquad (10)$$

Where, qe and qt are the amount of adsorbed (mg/g) at equilibrium and at time t (min). k_1 (min^{-1}) and k_2 (g/mg.min) are the pseudo-first and pseudo-second order rate constants, respectively. a_E is the initial adsorption rate (mg/g.min), β_E is the desorption constant (g.mg) during any one experiment, V is the rate constant of power function(min^{-1}) and k is constant of power function model (mg/g).

Results

Characterization of adsorbent

Fig. 1 shows the FTIR of prepared Peganum Harmala Seeds (PHS).

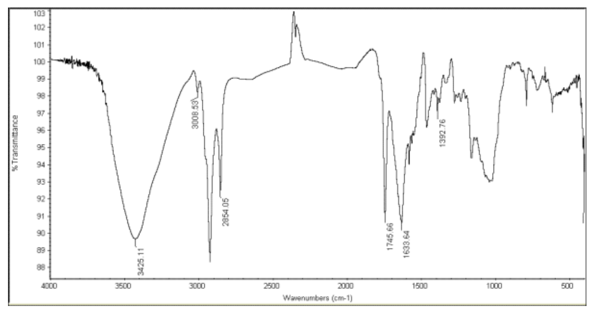

Figure 1) FTIR of Peganum Harmala Seeds

Fig. 2 shows the SEM image of PHS in different scales.

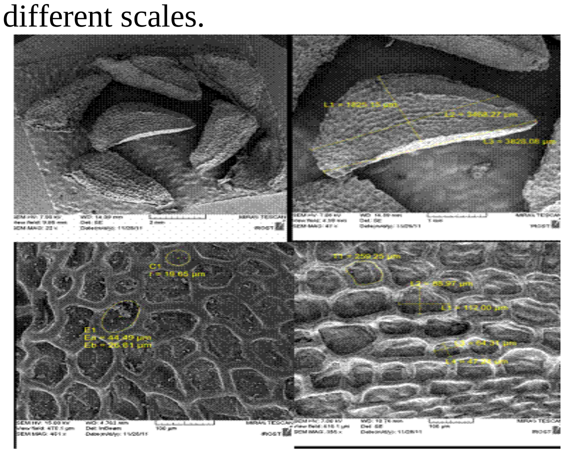

Figure 2) SEM of Peganum Harmala Seeds

Effect of contact time

The effect of contact time on the removal of heavy metals was studied and the result is shown in Fig. 3.

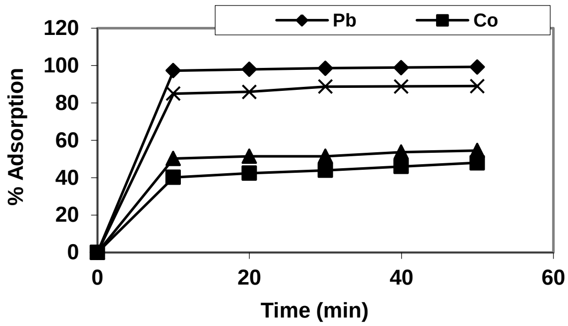

Figure 3) Effect of contact time
(PHS)=8g/100mL, (Pb)=50 mg/L, (Cu)= 50 mg/L; (Ni)= 50 mg/L; (Co)= 50 mg/L; pH=5;T=25°C

Effect of pH

The pH of solution was set in the range of 1-8. The results of the effect of pH on the heavy metals removal is shown in Fig. 4.

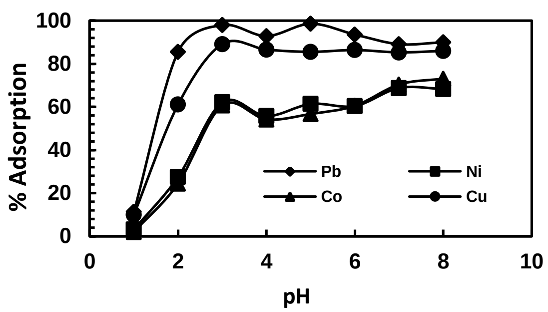

Figure 4) Effect of pH
(PHS)=15g/100mL, (Pb)=50 mg/L, (Cu)= 50 mg/L; (Ni)= 50 mg/L; (Co)= 50 mg/L; pH=5;T=25°C; Flow=1.8 mL/min

Effect of adsorbent dosage

The effect of adsorbent dosage on removal efficiency of heavy metals was studied (Fig. 5).

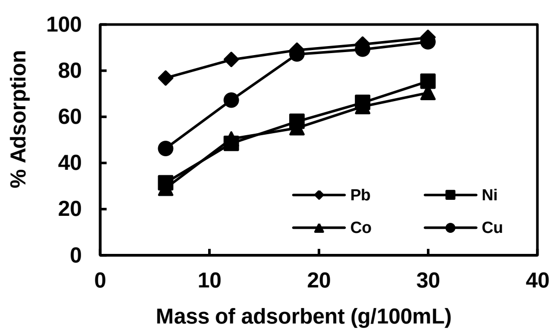

Figure 5: Effect of adsorbent dosage
(Pb)=50 mg/L, (Cu)= 50 mg/L; (Ni)= 50 mg/L; (Co)= 50 mg/L; pH=5;T=25°C; Flow=1.8 mL/min

Effect of heavy metals initial concentration

The effect of heavy metals initial concentration in removal of them by PHS is shown in Fig. 6.

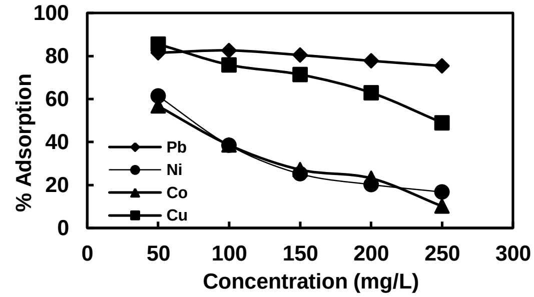

Figure 6) Effect of heavy metals initial concentration
(PHS)=15g/100mL, pH=5;T=25°C; Flow=1.8 mL/mim

Effect of ionic strength

To study the effect of ionic strength on adsorption of heavy metals onto PHS, sodium nitrate, sodium chloride and potassium chloride were used.

Effect of Particle Size

To study the effect of particle size, different size of PHS was used (0.5-1 mm, 1-2 mm and 2-3 mm). Table 1 shows the effect of particle size on removal of heavy metals by PHS.

Desorption study

Desorption of heavy metals from the surface of PHS was investigated, using water and various acids such as HCl, H_2SO_4 and HNO^{-3}.

Isotherm studies

The calculated results of adsorption of Pb^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} on the PHS as a function of the initial concentration of Pb^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} are shown in Table 2.

The results of the kinetic parameters for heavy metals adsorption onto PHS are listed in Table 3.

Table 1) The effect of particle size
(heavy metals)=50 mg/L; (Adsoebent)=15g/100 mL; pH=5; Flow= 3 mL /min

Size (nm)	Pb	Ni	Co	Cu
0.5-1	99.27	66.92	67.65	93.10
1-2	95.32	61.53	61.54	93.45
2-3	94.88	56.53	58.31	71.1

Table 2) The isotherm constants along with the correlation coefficients

	Isotherm									
	Langmuir				**Freundlich**			**Temkin**		
(Mn^+)	**qmax(mg/g)**	**b(L/mg)**	**R_L**	**R^2**	**Kf(mg/g)**	**n**	**R^2**	**a(L/g)**	**b(kJ/mol)**	**R^2**
Pb^{2+}	1.827	0.0274	0.4264	0.9413	23.286	0.9880	0.9585	2.267	7.477	0.8380
Ni^{2+}	0.4757	0.0238	0.4469	0.9112	60.187	1.356	0.9491	5.748	19.724	0.9091
Co^{2+}	1.037	0.0089	0.7035	0.9566	99.518	1.152	0.9219	6.669	19.369	0.9159
Cu^{2+}	1.0675	0.035	0.3726	0.9326	22.967	1.245	0.8847	2.356	11.717	0.7886

Table 3) Kinetic parameters for heavy metals adsorption onto PHS

	R^2			
M^{n+}	**pseudo-first order**	**pseudo-second order**	**Elovich**	**power function**
Pb^{2+}	0.826	1	0.969	0.969
Ni^{2+}	0.969	0.999	0.875	0.865
Co^{2+}	0.983	0.998	0.880	0.871
Cu^{2+}	0.892	1	0.865	0.865

Discussion

FTIR analysis of PHS confirmed the active groups on the surface of PHS. Adsorption peak of –NH and –OH (3425 cm^{-1}), stretching =C-H (2921 cm^{-1}), -CH (2854 cm^{-1}), -C=C and –C=N (1633 cm^{-1}), -C=O (1745 cm^{-1}), C-O (1392 cm^{-1}) were observed on the prepared PHS. These peaks confirmed the active groups on the PHS. As shown in Fig. 2, the surface of PHS is porous and satisfies as a good adsorbent for removal of heavy metals. Also, PHS particles are spherical in shape with rough Surface. EDAX analysis declared that it consists of 51.31% C, 7.11% H, 4.64% N and 36.81% O.

The results of contact time showed due to more availability of areas, the percentage removal of ions is higher at the beginning. By increasing the time, saturation of adsorbent surface with heavy metals decreased the removal efficiency. As results, Equilibrium contact time was reached for all of ions removal within 30 min, using PHS (19).

As shown, the removal of heavy metals is enhanced by increasing of pH. In fact, at lower pH the competitive hydrogen ions will compete with heavy metal ions for the active site. So, the percent of adsorption is decreased (20).

The obtained data showed that the amount of ions varied with varying the adsorbent dosage. Results show that removal of heavy metals from aqueous solution increased by increasing the adsorbent dosage (21). In fact, increasing adsorbent dose due to the increase of surface area provides more binding sites for the adsorption (16). Also, biosorbents contain some organic functional groups on their surface (alcohol, aldehydes, ketones, carboxylic, phenolic, and ether groups) and can ionize in aqueous solution and adsorbed cations (22-23).

Study the effect of initial concentration on removal efficiency indicated that by increasing the initial concentration of heavy metals, the removal efficiency was decreased (Fig. 6). In fact, there are limited adsorption sites on the adsorbent surface and at high concentration, it become saturated (24).

As results, all of heavy metals adsorption decreased by increasing of salts concentration (not shown). The decrease in heavy metals adsorption by increase of salts concentration, could be attributed to increase of heavy metal ions and cations competition for adsorption onto PHS (25). Also, the percent removal of pb^{2+} is more than other cations. Probably, pb^{2+} tended to adsorb strongly onto PHS (26).

According to Table 1, removal of heavy metals increased by decreasing of particle size. In fact, by decreasing of particle size, the contact of surface area was increased that duo to increase in heavy metals removal (27).

In comparison with acids, desorption of heavy metals by water is scanty. The data confirmed that acidic medium constitutes the better desorption reagent than water as to compete of hydrogen ions with metal ions. In addition, it was found that by increasing acid volume, desorption of heavy metals from the PHS surface was increased.

It is found that the adosorption of Pb^{2+} and Ni^{2+} on the PHS is correlated well with the Freundlich equation that suggested that there is a multi- layer uptake of the heavy metals and heterogeneous energetic distribution of the active binding sites on the biomass as well as interactions between the adsorbed molecules (20).

Adsorption of Co^{2+} and Cu^{2+} on the PHS is correlated well with the Langmuir equation, meaning that there is a mono- layer uptake of the heavy metals on a homogeneous surface was occurred and there is uniform energies of adsorption for all binding sites without any interaction between the adsorbed molecules (20) .

As results, kinetic of all heavy metals adsorption onto PHS is obeyed pseudo- second order kinetic.

Conclusion

Peganum Harmala Seeds are effective adsorbent for removal of Pb^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+} ions from aqueous solutions onto PHS followed pseudo-second order kinetic model. Isotherms studies show that experimental data can be described by the Langmuir isotherm for Co^{2+} and Cu^{2+} ions and Freundlich isotherm for Pb^{2+} and Ni^{2+} ions. FTIR spectra of PHS indicated that –NH, –OH, =C-H, -CH, -C=C, –C=N, -C=O and C-O were observed. Additionally, based on these finding, it is deduced that Peganum Harmala Seeds are relatively more effective for the removal of Pb^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+} ions from aqueous solutions in continuous solutions.

Footnotes

Conflict of Interest:

The authors declared no conflict of interest.

References

1. Argun ME, Dursun S, Ozdemir C, Karatas M. Heavy metal adsorption by modified oak sawdust:

Thermodynamics and kinetics. J Hazard Mater 2007;141(1):77–85.
2. Rafatullah M, Sulaiman O, Hashim R, Ahmad A. Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. J Hazard Mater 2009;170(2-3):969–977.
3. Perić J, Trgo M, Vukojević Medvidović N. Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms. Water Res 2004;38(7):1893-1899.
4. Kaczala F, Marques M, Hogland W. Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto Pinus sylvestris sawdust. Bioresou Technol 2009;100(1):235–43.
5. Meena AK, Kadirvelu K, Mishra GK. Rajagopal C, Nagar PN. Adsorptive removal of heavy metals from aqueous solution by treated sawdust (Acacia arabica). J Hazard Mater 2008;150(3):604-11.
6. WHO. Guidelines for Drinking-water Quality. 3 rd ed. Geneva: WHO; 2006.
7. Yu B, Zhang Y, Shukla A, Shukla SS, Dorris KL. The removal of heavy metals from aqueous solutions by sawdust adsorption- removal of lead and comparison of its adsorption with copper. J Hazard Mater 2001;84(1):83–94.
8. Gode F, Atalay ED, Pehlivan E. Removal of Cr(VI) from aqueous solutions using modified red pine sawdust. J Hazard Mater 2008;152(3):1201-7.
9. Bansal M, Singh D, Garg P. Use of agricultural waste for the removal of nickel Ions from Aqueous Solutions: Equilibrium and Kinetics Studies. Int J Civil Environ Eng 2009;1(2):108-14.
10. Qaiser S, Saleemi AR, Mahmood Ahmad M. Heavy metal uptake by agro based waste materials. Electron J Biotechnol 2007;10(3):409-16.
11. Al-Masri MS, Amin Y, Al-Akel B, Al-Naama T. Biosorption of cadmium, lead and uranium by powder of poplar leaves and branches. Appl Biochem Biotechnol 2010;160(4):976-87.
12. Nameni M, Alavi Moghadam M, Arami M. Equilibrium adsorption of hexavalent chromium from water using rice bran. Int J Environ Sci Tech 2008;5(2):161-8.
13. Taty-Costodes VC, Fauduet H, Porte C, Ho Y-S Removal of lead (II) ions from synthetic and real effluents using immobilized Pinus sylvestris sawdust: Adsorption on a fixed-bed column. J Hazard Mater 2005;123(1):135-44.
14. Habib A, Islam N, Islam A, Alam AS. Removal of Copper from Aqueous Solution Using Orange Peel, Sawdust and Bagasse. Pak J Anal Environ Chem. 2007;8(1):21-25.
15. Wilke A, Buchholz R, Bunke G. Selective biosorption of heavy metals by algae. Environ Biotechnol 2006; 2(2):47-56.
16. Yari AR ,Siboni Shirzad M ,Hashemi S, Alizadeh M, Removal of Heavy Metals from Aqueous Solutions by Natural Adsorbents (A Review), archives of hygiene sciences 2013; 2(3) :79-89.
17. Shamohamadi Heidari Z, Khajeh M. A Study on the Effects of Dosage Variation of Sawdust as an Absorbent on Uptake Kinetics of Hexavalent Chromium in Aqueous Solutions. J Environ Stud 2011;36(56):61-68.
18. Mehrizad A, Aghaie M, Gharbani P, Dastmalchi S, Monajjemi M, Zare K. Comparison of 4-Chloro-2-nitrophenol Adsorption on Ssingle-walled and Multiwalled Carbon Nanotubes. Int J Env Health Eng 2012;9(1):5-11.
19. Hlihor RM, Diaconu M, Fertu D, Chelaru C, Sandu I, Tavares T. Bioremediation of Cr(VI) Polluted Wastewaters by Sorption on Heat Inactivated Saccharomyces cerevisiae. Biomass 2013;7(3):581-594.
20. Jaafarzadeh N, Mengelizadeh N, Takdastan A, Heidari Farsani M, Niknam N, Aalipour M, et al. Biosorption of heavy metals from aqueous solutions onto chitin. Int J Env Health Eng 2015;4(1):1-7.
21. Naghizadeh A, Yari AR, Tashauei HR, Mahdavi M, Derakhshani E, Rahimi R, et al. Carbon nanotubes technology for removal of arsenic from water. Arch Hyq Sci 2012;1(1):6-11.
22. Gupta S, Babu BV. Modeling simulation and experimental validation for continuous Cr(VI) removal from aqueous solutions using sawdust as an adsorbent. Bioresou Technol 2009;100(23):5633–5640.
23. Agoubordea L, Naviab R. Heavy metals retention capacity of a non-conventional sorbent developed from a mixture of industrial and agricultural wastes. J Hazard Mater 2009;167(1):536–544.
24. Cheragi M, Sobhanardakani S, Lorestani B, Zandipak R. Tea wastes effeciency on removal of Cd (II) from aqueous solutions. Arch Hyq Sci 2016;5(3):184-191.
25. Doula M, Ioannou A, Dimirkou A. Thermodynamics of Copper Adsorption-Desorption by CA Kaolinite. Adsorption 2000;6(4):325-335.
26. Srivastava P, Singh B, Angove M. Competitive adsorption behaviour of heavy metals onto kaolinite. J Colloid Interface Sci 2005;290(1):28-38.
27. Chakravarty P, Sarma NS, Sarma HP. Removal of Lead (II) from Aqueous Solution using Heartwood of Areca Catechu Powder. Desalination 2010;256(1-3):16-21.