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Evaluation of factor affecting adsorption of Pb(II) by iron modified pomegranate peel carbons using factorial design

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ABSTRACT

Lead is one of the heavy metals, highly toxic to humans and can cause damaging effects even at very low concentrations. It is necessary that the high concentration of lead in aquatic decrease to permissible level. Carbonized pomegranate peels modified with iron have been investigated for removal of Pb(II) ions from aqueous solution. The effective factors were optimized by batch adsorption using factorial design approach to obtain the best model Pb(II) biosorption. All experiments were performed at Lab temperature (25ºC), contact time 90 min, and initial pH of 6.5. The 54 experiment designing of factorial design were done for optimization conditions. Maximum removal efficiency was calculated as 80.1% and 90.4%for Fe^{3+} andFe^{2+}impregnated pomegranate peel carbons respectively. Mass adsorbent was found as the most significant factor with F= 25.657 and P = 0.001 at 0.05% significant level. The results described in this study showed that carbonized pomegranate peels impregnated with Fe^{2+}ions had high removal efficiency for treatment of Pb(II) from waters and developed a model to predict Pb(II) removal in a batch biosorption process.

Keywords: Iron modified carbon; Factorial design optimization; pomegranate peels; Pb(II)

INTRODUCTION

Some heavy metals, like Fe, Zn, Ca and Mg, have been reported to be of necessary to man and their daily intake had been recommended. However, some others, like As, Cd, Pb, and Hg, have been reported to have no consumption even at very low concentrations can be toxic. They tend to accumulate in the food chain and in the body and can be stored in soft tissues such as kidney and hard tissues such as bone[1]. Lead inorganic forms are absorbed through ingestion by food and water, and inhalation. It causes inhibition of the synthesis of hemoglobin; dysfunctions in the kidneys, joints and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system and peripheral nervous system[2-4].WHO and EPA have established permissible value of 0.05 mg/l for lead in drinking water.

Among different technologies of purification, absorption has been attended to as a fast, cheap and efficient method[5].Adsorption process in batch systems usually depends on several factors such as pH of solution, adsorbent dose, initial metal concentration, contact time, temperature, etc. Many researchers tried to optimize the effective parameters on adsorption process[6-9].In their optimization procedures, one factor has been usually variable at a time and the other factors fixed. Subsequently, at optimum value of first factor, the other factor changes and continues to optimize all experimental parameters. This method of optimization is very time-consuming and needs to do many experiments. Also, the interactions among all factors are neglected[10]. It is further impossible to detect the frequent interactions which occur between two or more factors. Optimization by design of experiments (DOE) procedure involves changing all variables from one experiment to the next. The advantage of this procedure is that the influences of parameters are considered and the best values are obtained.

Until now, the use of industrial and agriculture wastes as adsorbent have been explored for removal of Pb(II) ions from aqueous solutions[11-15]. Pomegranate peels as an industrial waste produced in large scales in Iran. Pomegranate fruits are widely processed into juice, jams, syrup and sauce. The non edible portion (peel) of fruit is about 40–45% of the total fruit weight. Therefore, the idea to change the wastes of pomegranate manufacturing products to activated carbon for cleaning the environment is valuable. Previous study by El-Ashtouky et al. used the raw pomegranate peel, activated carbon prepared from pomegranate peel (AC1), and chemically-treated pomegranate peel (AC2) for removal of lead(II) and copper(II) from aqueous solution[16]. Ertas and Ztrk studied removal of lead from aqueous solution by chestnut shell adsorbent. They applied two-level factorial design to investigate the effects and interactions of parameters on Pb(II) removal and found that the adsorbent dosage, stirring speed, and pH had a positive effect on the adsorption[17]. Kadak applied full factorial design to study the removal of lead from aqueous solution by precipitation. Their results showed that the precipitation time had the greatest effect on removal efficiency[18].

The main objectives of this research were to modify of pomegranate peel carbons surface by treatment with Fe^{2+} and Fe^{3+} ions and to increase of their abilities for removal of Pb(II) ions from aqueous solution. An additional objective was to develop a model using full factorial design methodology that can be used ac a foundation for Pb(II) biosorption has been demonstrated.

EXPRIMENTAL SECTION

Reagents

All chemicals used for experiments were of analytical grade. The stock solution of 1000 mg/lPb(II) ions was prepared from $Pb(NO_3)_2$indeionized water and used for optimization experiments after dilution. $FeCl_3$ and $FeCl_2$ 0.1 M solutions were used for treatment pomegranate peels. Standard solutions for determination of Pb by flame atomic absorption spectrometry in the range of 0–50 mg/l were prepared from the stock standard solutions of 1000 mg/l through dilution with 1% (v/v) HNO_3.

Statistical design of experiments (DOE)

For quantification of the effects of the three variables on the Pb(II) biosorption, three levels of each factor were optimized by factorial design as 3^3 full factorial designs for two adsorbents include 54 experiments for Pb(II) biosorption. The order in which the experiments were conducted was randomized to avoid systematic errors. The coded values of variables 1, 2 and 3 in the adsorption of Pb(II) for solution volume (V), initial Pb concentration (C), and mass of adsorbent (m) are given in Table 1.

Table 1 The coded values and ranges of variables for adsorption of Pb(II) from aqueous solution

Factors	Name	Type	Level		
			1	2	3
Ads	Type of biosorbent	Qualitative	Fe^{2+}-PPC	Fe^{3+}-PPC	-
m	Biosorbent dose (w/v%)	Quantitative	0.1	0.5	1
C	Pb concentration (mg/l)	Quantitative	10	50	100
V	Solution volume (ml)	Quantitative	50	100	150

Preparation of adsorbents

Pomegranate peels were prepared from Nodoushan gardens at Yazd province, center of Iran. They were washed three times with water, dried at room temperature in absence of sunlight and sieved in the size range of 0.6–2.0 mm. To modify biosorbents, 20 g of dried granule was socked with 20 ml of 0.1 M $FeCl_3$ and $FeCl_2$solutions at 25 ºC for 24 h, separately. Then, the granules were carbonized at a temperature of 400ºC for 3h in a programmable furnace in the atmosphere of nitrogen. The mixture was washed several times with distilled water to remove any excess ions from the treated pomegranate peels. Finally, the iron modified pomegranate peel carbons were dried at 100 ºC and kept for further use.

Batch adsorption studies

Batch adsorption experiments were conducted by closed containers using Orbital shaker at 150 rpm and Lab temperature (25 ºC). According to the DOE, the 54 experimental conditions were performed to achieve the optimization condition in the closed containers. After reaching to equilibrium, the solids were separated using filters and the absorbance of the clear liquid was analyzed by flame atomic absorption spectrometry at maximum wavelength of 283.3 nm. Control samples without biosorbent were run in parallel. All of the experiments were carried out at initial pH solution of 6.5 and fixed shaking time of 90 min for 3 replicates.

Data analysis

The remaining concentration of Pb(II) in clear solution was recorded three times in a standard mode and concentration of Pb ions in aqueous solution was calculated from Beer-Lambert equation. The adsorption efficiency of iron modified PPC was calculated from experimental data as equation 1.

$$\%\,\mathrm{RE} = \frac{(C_0 - C)}{C_0} \times 100 \qquad (1)$$

The results of the experimental design were analyzed using MINITAB 16 software to evaluate the effects, coefficients, standard deviation of coefficients. Common statistical tools, such as F-test and t-test, were used to define the most important variables affecting the lead adsorption efficiency. The interactions between independent factors were determined by analysis of variance (ANOVA) and the main effects of parameters on the Pb(II)biosorption were identified based on the p-value=0.05 of confidence level.

RESULTS AND DISCUSSION

SEM of biosorbents

The SEM images of the PPC and iron modified PPC were studied and represented in Fig 1 (a) and (b), respectively. The comparison of images illustrated that the untreated PPC has regular surfaces with low porosity particles, whereas in iron modified PPC biosorbent the number of particles on surface increased and their porosity developed, consequently the active surfaces of carbon particles has been enhanced.

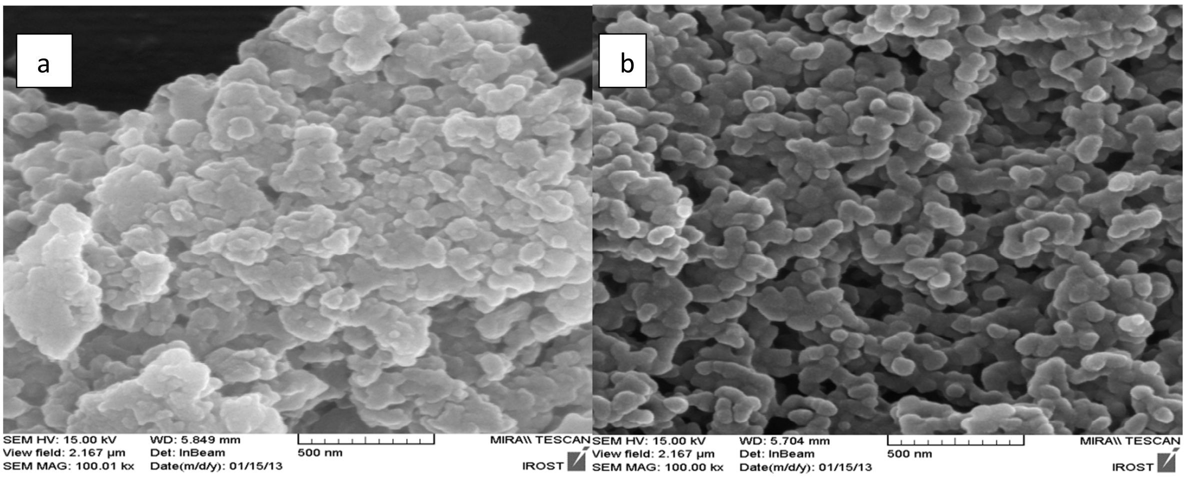

Fig 1: SEM images (a) PPC (b) iron modified PPC

Table 2 Estimated regression coefficients and analysis of variance for Pb(II) adsorption on Fe^{2+}-PPC

	Statistic						
Factors	D.F	Coeff	SE Coeff	SS	MS	F	P
Constant	9	35.93	46.22	1423.7	1581.8	7.60	0.448
m	1	62.95	26.57	9512.8	1169.5	5.62	0.030
C	1	2.25	26.57	419.5	1.5	0.01	0.933
V	1	-51.88	26.57	2706.0	794.2	3.81	0.067
m. m	1	-11.53	5.98	798.1	798.1	3.83	0.067
C.C	1	-3.08	5.89	57.0	57.0	0.27	0.607
V.V	1	10.18	5.89	622.2	622.2	2.99	0.102
m. C	1	3.13	4.17	117.8	117.8	0.57	0.462
m. V	1	-0.05	4.17	0.0	0.03	0.00	0.199
C.V	1	-0.51	4.17	3.1	3.1	0.01	0.904
Error	17			3540.0	208.2		

Optimization of adsorption process by factorial design

Factorial design is employed to achieve the best overall optimization of the system. It was used to reduce the time, overall process cost, and to obtain better response [19]. The design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors. The number of experimental runs at n levels is n^k, where k is the number of factors [20].In our procedure,27 possible combinations were obtained for three variables with three levels for each variable in the experimental design matrix. Totally, 54 combinations were performed because each experiment was done for two adsorbents. The range levels (Table 1) for the factors were selected according to some preliminary experiments.

The results of experimental design were interpreted along with analysis of variance (ANOVA) and linear regression model. The statistical plots, the main effects, and interactions between factors were estimated with the Minitab 16 software. The results of the linear regression and analysis of variance for Fe^{2+}-PPC and Fe^{3+}-PPC are presented in Table 2 and Table 3, respectively.

Table 3 Estimated regression coefficients and analysis of variance for Pb(II) adsorption on Fe^{3+}-PPC

	Statistic						
Factors	D.F	Coeff	SE Coeff	SS	MS	F	P
Constant	9	59.06	5.61	9960.4	1106.7	9.11	0.000
m	1	19.52	2.60	6860.1	6860.1	56.50	0.000
C	1	3.50	2.60	221.2	221.2	1.82	0.195
V	1	-10.35	2.60	1928.2	1928.2	15.88	0.001
m. m	1	-6.24	4.50	234.0	234.0	1.93	0.183
C.C	1	-8.86	4.50	471.1	471.1	3.88	0.065
V.V	1	0.90	4.50	4.9	4.9	0.04	0.843
m. C	1	-2.64	3.18	83.7	83.7	0.69	0.418
m. V	1	-3.61	3.18	156.2	156.2	1.29	0.272
C.V	1	0.28	3.18	0.9	0.9	0.01	0.932
Error	17			2064.3	121.4		

Analyses were done by means of F-test, and p-value. The F-test was used to determine the significance of the regression coefficients of the parameters. The p-values were used as tools to check the significance of each of the interactions among the variables, which in turn indicate the patterns of the interactions among the variables. In general, the larger the magnitude of F and the smaller the value of p, the more significant is the corresponding coefficient term [20, 21]. According to Fisher's F-test and p-value, the parameters adsorbent dose (m) and volume (V) were statistically significant for Pb(II) adsorption on two biosorbents, while the other interactions effects were statistically insignificant compared to the other effects. The interactions effects of m.m for Fe^{2+}-PPC and C.C for Fe^{3+}-PPC were statistically significant compared to the other interaction effects. Discarding the insignificant parameters instructs to following regression equation for Pb(II) adsorption efficiency on Fe^{2+}-PPC and Fe^{3+}-PPC:

$$\% \text{ Pb biosorption} = 35.93 + 62.95m - 51.88V - 11.53m.m \quad (\text{on } Fe^{2+}\text{-PPC}) \qquad (2)$$

$$\% \text{ Pb biosorption} = 59.06 + 19.52m - 10.35V - 8.86C.C \quad (\text{on } Fe^{3+}\text{-PPC}) \qquad (3)$$

The effects of individual variables and interaction effects can be estimated from the above equations. According to equations 2 and 3, mass of the biosorbent has a positive effect, while volume has a negative effect on Pb removal in the various ranges of each variable. In addition, mass of biosorbent has the greatest effect on Pb adsorption, followed by volume of solution and initial concentration, respectively. To confirm it, the main effects plots were generated to represent the results of regression analysis. The main effects represent the deviations of the average between high and low levels for each of them. When the effect of a factor is positive, adsorption efficiency increases as the factor is changed from low to high levels. In contrast, if the effects are negative, a reduction in adsorption efficiency occurs for high level of the same factor [22].

Fig. 2 shows the main effects of each parameter on the Pb(II) adsorption efficiency. It can be inferred that the biosorbent dose had strong positive influences upon adsorption process efficiency, thereby, increasing the biosorbent dose from 1 to 1.5 g in 100ml solution, increasing the Pb(II) adsorption. The other important main effect regarding the adsorption process was the effect of the volume of solution. It had a negative influence upon adsorption process efficiency, as its coefficient was the largest for two biosorbents studied. It means that Pb(II) adsorption was favored at low volume values. The initial concentration of Pb(II) also had a considerable effect on Pb(II) adsorption efficiency. An increase in initial concentration from 10 to 50 (level 1 to level 2) resulted in an increase in Pb(II) adsorption, while further increase to 100,induced a decrease in Pb(II) adsorption for the Fe^{2+}-PPC. An increase in initial concentration from level 1 to level 3 resulted in a decrease in Pb(II) adsorption for the Fe^{3+}-PPC. This difference has been presented in **Fig 2.**

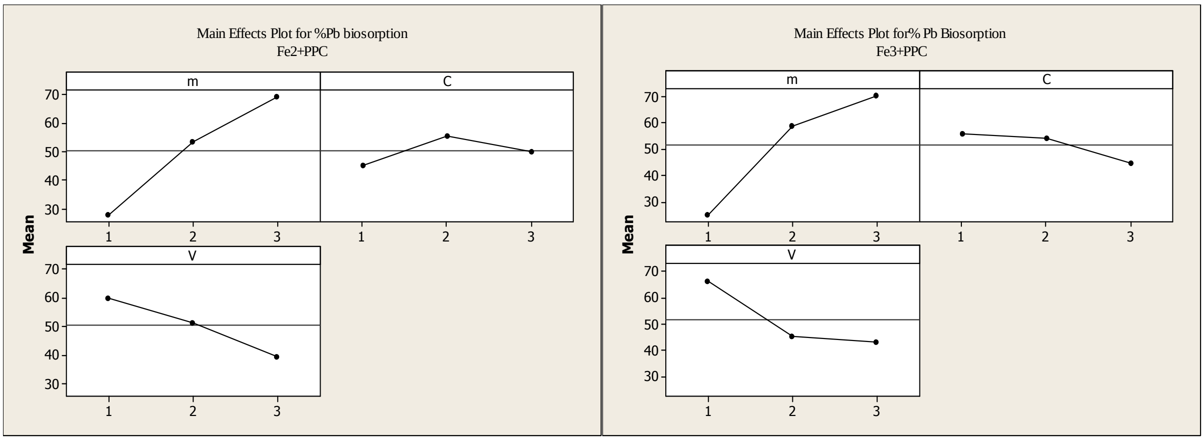

Fig. 2:Main effects of each parameter on the Pb(II) biosorption efficiency

The interaction effects of each parameter on the Pb(II) adsorption are shown in Fig. 3. Some lines in Fig. 3 are not parallel and present evidence for strong interactions among control factors. It is obvious that there is a significant interaction between volume of solution and initial Pb(II) concentration for adsorption efficiency on Fe^{2+}-PPC, at level 2. It was also observed for two biosorbents that the effect of C was more noticeable when the volume was high, but at higher biosorbent dose, the effect of initial concentration was insignificant.

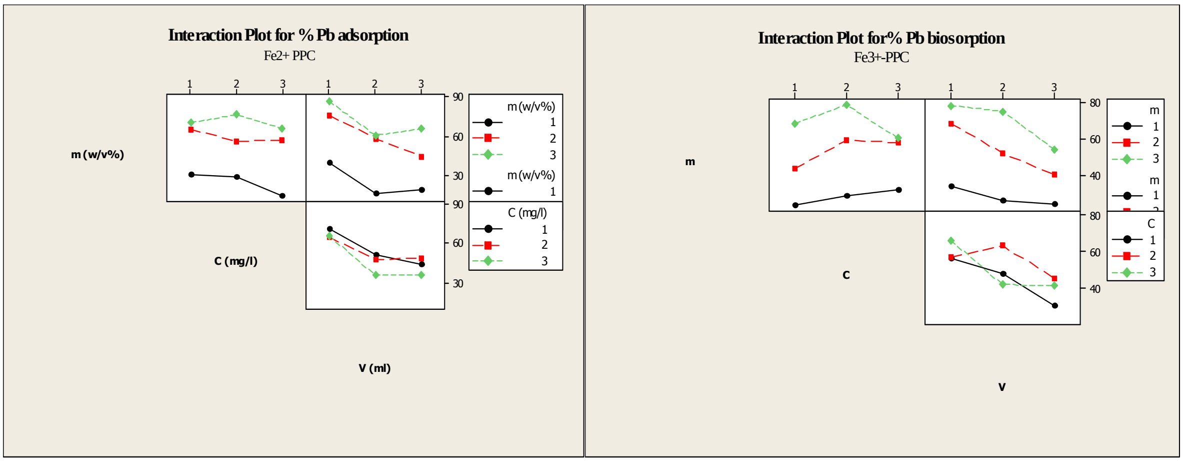

Fig. 3:Interaction effects of each parameter on the Pb(II) biosorption efficiency

According to the ANOVA analysis, the interaction between biosorbent dose and solution volume was insignificant. It means that the conclusion must be drawn very carefully, because the interaction can mask the main effects of the control factors.

CONCLUSION

The treatment of pomegranate peels in Fe^{2+} solutions and follow the carbonization at 400 °C modified their surfaces for adsorption of heavy metals. This methodology can be used to develop of cost-effective and environmental friendly for removing of heavy metal. Factorial design was employed to achieve the best overall optimization of system and the effects of parameters on each other. The results indicated the biosorbent dose had strong positive influences upon adsorption process efficiency. According to the ANOVA analysis, the interaction between biosorbent dose and solution volume was insignificant. It means that the conclusion must be drawn very carefully, because the interaction can mask the main effects of the control factors.

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