Efficient removal of lead(II) ions in water using functionalized poly(styrene) oligomers

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Abstract
In this research, chemically functionalized polystyrene oligomers with acrylamide monomers were applied as alternative adsorbent towards Pb(II) from aqueous solutions. Adsorption process of Pb(II) was optimized using the 2^{4-1} fractional factorial design with replicates at the central point supplemented with the central composite design where the percentage adsorption was chosen as the response variable. This variable was simultaneously optimized using the desirability functions approach to select the best conditions for the adsorption process. The experimental data reveal that after the optimization, the maximal response was exhibited at 38 °C, pH 5.80, initial adsorbate concentration (36.40 mg L^{-1}), and adsorbent dosage (10.77 mg) with the desirability function of 0.9260. Theoretical values and experimental data determined by the central composite design showed a high correlation with a R^2 value of 0.9810. Under these optimal conditions, the theoretical value for the removal of Pb(II) was 93.12%, while that experimental assay gives a maximum value of 91.23%. Likewise, the analysis of surface charge distribution, the structural and morphological characteristics confirmed the successful chemical modification of poly(styrene) oligomers.

Keyword: Oligomer, Adsorption, Response surface methodology, Central composite design, poly(styrene)

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1. Introduction

Adsorbent materials based on waste polymers such as polypropylene (PP)[1], polyethylene terephthalate (PET)[2] , poly(vinyl chloride) (PVC)[3] , polycarbonate (PC)[4], polyethylene (PE)[5] and poly(methyl-methacrylate) (PMMA)[6] have received great attention due to its low cost, high adsorption capacity, relatively easy regeneration, and the possibility to shape them into most suitable morphology-like spheres, fibers, films or membranes[7]. According to recently literature on the removal of heavy metals, various adsorbent based on organic and mineral structures, biological and polymeric materials have been used so far. In fact, we have recently demonstrated that introduction of acrylamide units inside of PS oligomer chains provide an interesting adsorbent material with a strong affinity for binding lead[8]. In spite of their demonstrated efficacy, the most of studies have been focused mainly on the study of adsorption properties and elucidation of adsorption mechanism while that optimization of variables that affect this process have been scarcely explored[9]. In this regarding, optimal adsorption conditions are prerequisite, particularly in the case of scaled up applications, to minimize cost and maximize the adsorption efficiency towards heavy metals. Classical optimization, in which only one factor is changed at a time with the purpose to measure its effect, takes a lot of time and requires a large number of experiments. Conversely, the response surface methodology, in which key parameters are simultaneously optimized, overcomes the deficiencies of single factor optimization. It is important to remark that using RSM substantially reduces the number of experiments necessary to predict the optimal adsorption conditions[10]. Moreover, modeling the process refines the interpretation of complex phenomena and provides a basis for process scaling. In this research, the adsorption process of Pb(II) from aqueous solution using an adsorbent material based on PS oligomers was simultaneously optimized using factorial design with the percentage removal as variable response. With the aim to select the best conditions for the removal of Pb(II), the 2^{4-1} factorial design with replicates at the central point was complemented with the central composite design with axial points to build a quadratic polynomial model and to investigate the response surface space.

2. Materials and methods

Synthesis and characterization of chemically modified PS oligomers and their preliminary adsorption studies have been already published[8]. Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer. The surface morphology was performed by field emission scanning electron microscope (FESEM) in a JEOL model JSM-6701F apparatus. Pb(II) ions from aqueous solutions were measured by flame atomic absorption spectroscopy (FAAS) on a Perkin Elmer PinAAcleTM 900F atomic absorption spectrophotometer. Batch adsorption experiments were carried out in a thermo scientific precision 270 circulating water bath. The point of zero charge (PH_{pzc}) of chemically modified PS oligomers was determined according to the procedure reported in the literature[11]. Blank test was simultaneously performed without chemically modified PS oligomers under the same conditions.

2.1 Experimental design

The best conditions for the removal of Pb(II) ions using chemically modified PS oligomers were determined using the 2^{4-1} fractional factorial design with center points supplemented with a face centered central design (FCCD)[12]. In our study, it is translated into 8 factorials and 8 axial points with 2 replicates at the central point, which gives a set of 18 experiments (Table 1), where the independent variables under analysis were pH (A), initial adsorbate concentration (B), adsorbent dosage (C) and temperature (D) (See table 2). Optimal conditions for adsorption experiments based on the Batch mode were determinate by using the optimal predictor quadratic model (1):

$$Y = b_o + \sum_{i=1}^{n} b_i x_i \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 \sum_{i=1}^{n} \sum_{j=i+1}^{n} b_{ii} x_i x_j \quad (1)$$

Where Y is the predicted response, b_o is the constant coefficient, b_{ii} are the quadratic coefficients, b_{ij} are the interaction coefficients, x_i *and* x_j are the coded factors of the independent variables considered for optimal conditions for adsorption of Pb(II) ions using chemically modified PS oligomers.

Table 1 Experimental design, experimental and predicted responses for removal of Pb(II) by Batch mode

Run	Coded factor				A	B	C	D	(%) Pb(II) Removal	
									Experimental	Predicted
1	0	0	0	+1	3.9	30	20	45	13.27	11.06
2	-1	0	0	0	2.0	30	20	35	28.40	26.19
3	+1	+1	-1	-1	5.8	50	10	25	63.48	62.91
4	0	0	0	0	3.9	30	20	35	16.50	23.13
5	+1	-1	+1	+1	5.8	10	30	45	13.52	15.20
6	-1	+1	+1	+1	2.0	50	30	45	7.86	9.54
7	+1	0	0	0	5.8	30	20	35	89.07	86.86
8	0	0	0	-1	3.9	30	20	25	20.47	18.26
9	0	0	0	0	3.9	30	20	35	15.93	23.13
10	+1	-1	-1	+1	5.8	10	10	45	57.42	56.85
11	-1	-1	-1	-1	2.0	10	10	25	19.38	18.81
12	+1	+1	+1	-1	5.8	10	30	25	60.04	61.72
13	-1	+1	-1	+1	2.0	50	10	45	9.96	9.39
14	-1	-1	+1	-1	2.0	10	30	25	7.80	9.48
15	0	0	+1	0	3.9	30	30	35	18.07	11.36
16	0	-1	0	0	3.9	10	20	35	6.74	4.53
17	0	0	-1	0	3.9	30	10	35	22.07	24.36
18	0	+1	0	0	3.9	50	20	35	19.38	17.17

On the other hands, the analysis of variance was used to measure the magnitude of the influence of the independent variables on the response factor. The adjusted determination coefficient (R^2_{Adj}) was used as a measurement of the proportion of the total observed variability described for 1. Quadratic models were used to build the surface response of the adsorption of Pb(II) ions and to find the maximum value of response by using the statistical software Design Expert 9.0.6.2 (Stat-Ease Inc., USA).

2.2 Adsorption experiments

The adsorption experiments were carried out in a batch method[13], which consists of shaking 20.0 mL of Pb(II) in stoppered glass tubes according to the adsorbent dosage, pH, temperature, and initial adsorbate concentration indicated in table 1. The coded factors and their actual levels are given in Table 2. The percentage of removal (%) was calculated by equation (1) as follows:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where C_o and C_e are the concentration at initial and equilibrium states (mg L^{-1}), respectively.

The equilibrium amount q_e (mg g^{-1}) adsorbed per unit mass of adsorbent material was evaluated using equation (3):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (3)$$

Where q_e is the equilibrium amount of Pb(II) adsorbed per unit mass, V (L) is the volume of solution and W (g) is the mass of chemically modified PS oligomers.

Table 2 Independent variables and coded levels used in the experimental design

Independent variable	Coded factor	Unit	Coded levels		
			Low -1	Center 0	High +1
			Actual levels		
pH	A	u.a	2.0	3.9	5.8
Initial adsorbate concentration	B	mg L^{-1}	10	30	50
Adsorbent dosage	C	mg	10	20	30
Temperature	D	°C	25	35	45

3. Results and Discussion

3.1 Physical chemical properties

The adsorption of toxic metals from aqueous solutions depends on various factors such as pH, temperature, equilibrium time, initial absorbate concentration and adsorbent dosage. In specially, the removal of toxic metals depends highly on the pH of solution. To determine the pH at which chemically modified oligomer surface is neutral; the point of zero change (pH_{pzc}) of this adsorbent was determined as can be seen in fig. 1. It is evident from fig. 1 that the pH_{pzc} of chemically modified PS oligomers is 5.63. According to this value, the adsorbent material can be considered acidic[14]. The experimental results given in table 1 indicate that the percentage adsorption increase by increasing pH from 2.00 to 5.80. This behavior could be attributed to the fact that at higher pH, the acrylamide units linked to PS oligomers would favored the protonated form, which will increase the number of protonated species and generates the electrostatic repulsion forces among the adjacent protonated terminal amide groups (See Scheme 1) . A similar tendency has been reported by Sarkar *et al.,*[15] for removal of malachite green dye using biodegradable graft copolymer derived from amylopectin and poly(acrylic acid). The author found that at pH > pH_{pzc} of adsorbent, the electrostatic attraction between negatively charged surface of adsorbent and positively charged adsorbate is enhanced, resulting in high malachite green dye removal.

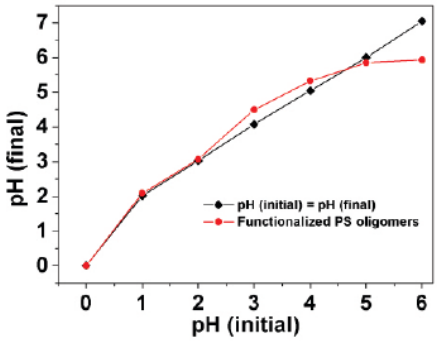
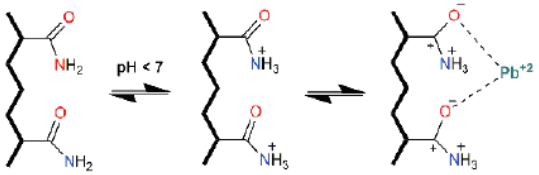


Fig. 1 pH drift method to obtain pH_{PZC} value for functionalized PS oligomers.



Scheme 1. Schematic representation of chemically modified PS oligomers (-) with acrylamide monomers and proposed adsorption mechanism.

3.2 Spectroscopic and morphology characterization

Fig. 2 shows a comparison of infrared spectra between chemically modified PS oligomers (a), PS oligomers (b) and virgin PS(c). The infrared spectra of chemically modified oligomers clearly show a stretching band at 1660 cm^{-1} due to the amide groups, which corroborates the formation of covalent bond present in the PS oligomer chains. The FESEM image analysis of PS oligomers and chemically modified PS oligomers are given in fig. 3. The micrograph analysis revealed that PS oligomers (Fig. 3a) exhibit many pores throughout the surface, while functionalized PS oligomers (Fig. 3b) show the formation of spherical aggregates with a wide distribution of sizes, and an apparent low porosity due to introduction of acrylamide units inside oligomer chains.

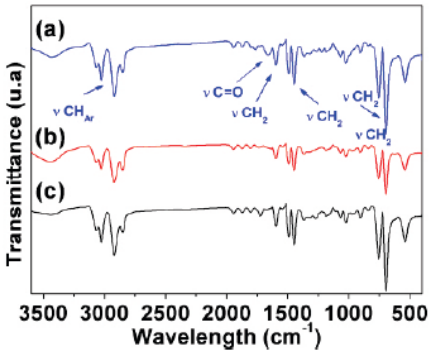


Fig. 2 Infrared spectra of (a) functionalized polystyrene oligomers; polystyrene oligomers (b); and (c) virgin polystyrene in the 3600–400 cm^{-1} region.

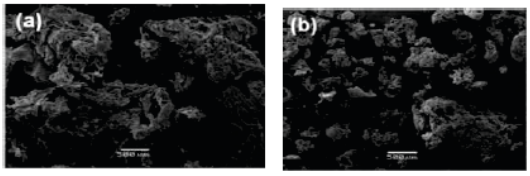


Fig. 3 FE-SEM images of free oligomers (a) and functionalized PS oligomers (b).

3.3 Statistical analysis

With the aim to determine the ideal conditions for the removal of Pb(II), the effect of four adsorption variables were studied using central composite design (CCD) and response surface methodology (RSM). The analysis of variance (ANOVA) used to determine the significance of curvature for absorption of Pb(II) ions at a confidential level of 95% is given in table 3. The analysis of these data revealed that the curvature is significant, which means that there is an inflection point on variable set under study. Hence, the linear model is not able to represent the design space and, for this reason, FCCD design was selected to fit the quadratic model considering the 18 experimental runs.

According to the ANOVA data for removal of Pb(II), the pH resulted to be the most important quadratic term as well as the most significant individual factor while that adsorbent dosage ($p = 0.0768$) and initial adsorbate concentration ($p = 0.0863$) exhibited both less significance for adsorption of Pb(II) ions in comparison with the pH (Eq. (3)). This is consistent with the results reported by Meenakshi *et al.* [16] for adsorption of Cd(II) and Pb(II) from aqueous solutions using poly(aniline) grafted chitosan copolymer as an adsorbent. In the case of other independent variables, double interactions as well as quadratic terms, the ANOVA analysis showed a non-significant with p-value in the 0.11–0.89 range. On base of these findings, we can assume that the binding of Pb(II) with chemically functionalized PS oligomers is dependent of pH, adsorbent dosage, and initial adsorbate concentration as was suggested by analysis of variance.

$$\text{Percentage of removal \%} = 23.13 + 30.34x_1 + 6.32x_2 + 4.14x_1x_2 + 0.92x_1x_4 + 6.24x_2x_3 + 11.65x_2x_4 + 3.87x_3x_4 + 33.39x_1^2 \quad (3)$$

The adjust determination coefficient (R^2_{Adj}) for removal of Pb(II) was 0.8924, which suggests that model could represent approximately 89.24% of the observed variability on the adsorption of Pb(II). Therefore, only 10.76% of the total variations can not explained by the mathematical model, which ensures the good adjust of the experimental data. The relationship between predicted and experimental values for the adsorption of Pb(II) is given in the fig. 4. The high correlation given for the quadratic model (R^2=0.9810) suggests a strong agreement between the predicted and experimental responses.

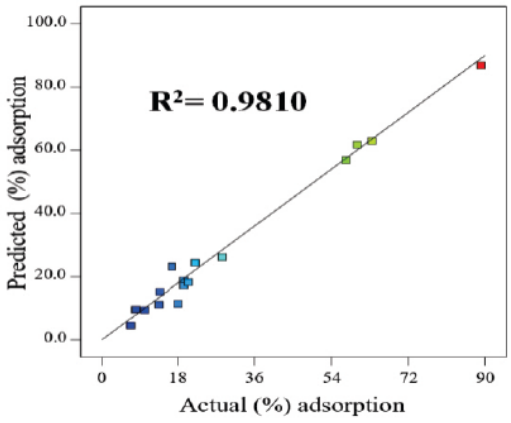


Fig. 4 Predicted against experimental data plots for adsorption of Pb(II).

On the other hand, the mathematical model was used to build response surface plots and investigate the interactions among the independent variables as well as determine the optimal condition of each factor for the maximum adsorption of Pb(II). Fig. 5a) shows that the percentage removal of Pb(II) is increased at pH values above 5.26 when the adsorbent dosage and initial adsorbate concentration are fixed. Moreover, fig. 5 b) and c) show that at adsorbent dosage below of 10 g and temperatures above 35°C, the percentage adsorption of Pb(II) ions exhibits remarkable decrease.

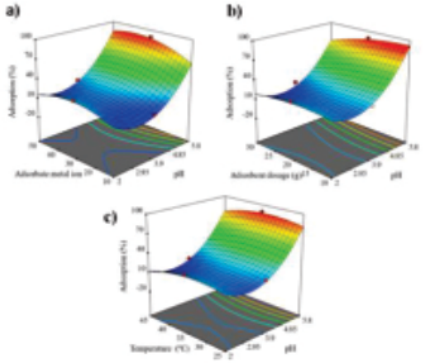


Fig. 5 Response surface plots for adsorption of Pb(II) from aqueous solutions.

3.4 Optimization of Batch adsorption mode

To determine the optimal conditions, equation (3) was used to maximize the percentage removal of Pb(II). Under these conditions, the maximum percentage removal of Pb(II) (93.12 %) was predicted to occur at 38 °C, pH 5.80, an initial adsorbate concentration of 36.40 mg L^{-1}, and an adsorbent dosage of 10.77 mg with a desirability function of 0.926. The analysis of response variable revealed that the percentage adsorption of metal ions is enhanced above pH 5.63 due to increase of electrostatic interactions between the surface of functionalized PS oligomers and positively charged ions. But if the temperature is lesser than 35°C, a decrease on the percentage adsorption of Pb(II) could be attributed to low mobility of heavy metals ions. On the contrary, at temperatures greater than 35°C, the percent of adsorption is reduced because increasing the kinetic energy decreases the efficiency of the removal process. Likewise, the effect of the initial adsorbate concentration on the percentage adsorption at concentrations below to 10.74 mg L^{-1} shows that the active sites on the adsorbent material are not completely occupied. Thus, the interaction of heavy metal ions through the surface is not enhanced, decreasing percentage removal. To validate the predicted response, experimental assays were carried out at the optimal conditions giving a percentage removal of Pb(II) equal to 91%, which is similar or greater than other adsorbent materials derivatives from waste polymers (Table 4).

Table 4 Comparison of the key parameters for the removal of Pb(II) by chemically functionalized polymers.

Waste polymer	Monomer	pH	Adsorbate concentration [mg L^{-1}]	Adsorbent dosage [mg]	Temperature [°C]	(%) Pb(II) Removal	Reference
PS	Tpy	7.00	1000	100	25	80	17
PP	VIm/AN	N.R	N.R	100	N.R	78	18
PET	AA/Aam	8.00	250	15	25	100	19
PS	Aam	5.80	36.40	10.77	38	91	This work

Tpy, terpirydine; VIm, Vinylimidazole; AN, aniline; AA, acrylic acid; AAm, acrylamide.

Conclusions

In summary, this study demonstrated the usefulness of a central composite design to determine the optimal conditions to enhance the percent of removal of Pb(II) from aqueous solutions. After the simultaneous optimization by quadratic model, the optimal conditions were obtained at 37.71°C, an initial adsorbate concentration of 36.37 mg mL^{-1}, a pH of 5.80 and an adsorbent dosage of 10.75 g. At these conditions, the predicted response for the removal of Pb(II) was 93.12%, which is similar to the experimental value (91.23%). The percentage of removal determined under the optimal conditions by the simultaneous optimization showed a high percentage, which is similar or higher compared to with other adsorbent materials based on waste polymers. Lastly, the surface charge distribution, the structural and morphological features corroborate its successful obtention and confirm it is use as an inexpensive, efficient, and available adsorbent for removal of heavy metal from aqueous systems.

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