SYNTHESIS OF MGO NANOSTRUCTURES VIA SIMPLE SONOCHEMICAL METHOD FOR ADSORPTION OF LOW CONCENTRATIONS OF AMOXICILLIN FROM AQUEOUS PHASE

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Abstract - MgO nanostructures were synthesized through a simple sonochemical approach to be applied for removing low concentrations of amoxicillin from the liquid phase. As results, scanning electron microscopy (SEM) exhibited favorable structure for as-synthesized MgO nanostructures with low aggregation. In the following, adsorption of amoxicillin by MgO nanostructures was optimized via response surface methodology (RSM) based on central composite design (CCD). Accordingly, the maximum amoxicillin removal of 79.32% was obtained at amoxicillin concentration of 4.62 mg/L, reaction time of 73.78 min and MgO nanostructures dosage of 2.09 g/L. The results showed that increasing MgO nanostructures dosage and elapsed time, together with decreasing the initial amoxicillin concentration, favored the removal of amoxicillin through the adsorption process.

Keywords - Sonochemistry; Magnesium oxide; Nanoparticles; Adsorption; Antibiotic; Experimental design

I. INTRODUCTION

In resent decade, the application of nanotechnology for the environmental remediation has gained great attentions by many researchers. One of the most important environmental problems regarding water pollution is the release of pharmaceutically active compounds such as antibiotics into rivers and lakes. These compounds are recognized as refractory residues and classified as emerging pollutants [1]. Antibiotics are the main class of drugs consumed for the treatment of various bacterial infections. The release of antibiotics into the aqueous phase can cause toxicity toward algae and other aquatic organisms, even at very low concentrations. Among different antibiotics, amoxicillin has been identified as one of the most frequently consumed antibiotics[2]. Several treatment methods have been proposed and applied for the removal of amoxicillin from the liquid phase. However, the application of adsorption process is of great interest among researchers due to its low cost and simplicity in operation [1-4]. Prior to this, activated carbon has been extensively used as an efficient adsorbent for sequestring organic pollutants from water and wastewater [5]. In the present investigation, the application of a nanostructured adsorbent named magnesium oxide (MgO) has been considered in order to develop new alternative adsorbents for the decontamination of amoxicillin-contained water. The catalytic activity of MgO in nano-size has been proven in our previous studies for the degradation of organic compounds in the aqueous phase [6, 7]. However, in the present work, adsorptive characteristics of MgO nanostructures were examined for treating amoxicillin via the adsorption process. In a different manner, the process of amoxicillin adsorption by MgO nanostructures were evaluated by way of response surface methodology (RSM) based on central composite design (CCD) in order to optimize the operational parameters for the maximum efficiency. Moreover, this statistical approach is beneficial regarding economical point of view [5, 8, 9]. Design-Expert software was applied for the analyses of experimental data.

II. MATERIALS AND METHODS

A. Materials and Procedures

All analytical grade materials, which were used in the present research, were purchased from Merck, Germany. Double distilled water was applied for the preparation of stock solution and dilution of as-prepared solutions. Mg(NO3)2.6H2O was selected as the precursor of magnesium oxide (MgO) nanostructures. For synthesis of MgO nanostructures, 0.2 M of Mg(NO3)2.6H2O was prepared in a 100-mL distilled water solution. Then, 1 M of NaOH solution was added dropwise to the above solution to form a white precipitate under constant stirring. The resulting suspension was sonicated using an ultrasonic bath for 120 min at 50 °C. Afterwards, the suspension was repeatedly washed via distilled water and ethanol during the filtration. Finally, water content of the filtered sample was dried in an electric oven at 80°C for 24 h, generating MgO nanostructures [6, 7]. The adsorption experiments of amoxicillin were performed using Erlenmeyer flasks (100 mL) as batch flow-mode reactors. A shaker was implemented for the agitation of amoxicillin-contained solutions. The residual concentration of amoxicillin was determined using high performance liquid chromatography (HPLC). As-prepared nanostructures were characterized using a scanning electron microscope (TESCAN, Mira3, Czech Republic). Field emission scanning electron

microscopy (FE-SEM) was performed for morphological characterization.

B. Experimental design

To evaluate the effect of operational parameters on the adsorption of amoxicillin, three influencing parameters were selected as tabulated in Table 1. The number of experimental runs was computed using the following equation:

= 2 + 2 + (1)

where N is the number of experiments, k is the number of parameters (k=3) and x0 is the number of replications (x0=6) [8]. Accordingly, the number of experiments was obtained to be 20 runs (Table 2). The efficiency of the adsorption process for removing amoxicillin was estimated and predicted by the following second-order equation:

= + ∑ +(∑) + ∑ ∑ (2)

where Y is the predicted response (amoxicillin removal efficiency), b0 is a coefficient constant, bi is linear coefficient, bij is interaction coefficient and bii is quadratic coefficient. Besides, xi and xj are coded values of the parameters [1, 5].

Table 1. Experimental parameters together with their ranges and levels

Parameters	Ranges				
	−2	−1	0	+1	+2
Amoxicillin conc. (mg/L)	3	4.62	7	9.38	11
Elapsed time (min)	10	26.22	50	73.78	90
Adsorbent dosage (g/L)	0.5	0.91	1.5	2.09	2.5

III. RESULTS AND DISCUSSION

A. Morphological characterization

The result of FE-SEM analysis is depicted in Figure 1. As depicted, MgO nanostructures have been formed well in nano-size during the sonochemical synthesis. The size distribution of as-prepared nanostructures is ranged lower than 100 nm. They are relatively uniform in size. According to the taken image, sonochemical synthesis of nanostructures resulted in no aggregation of as-prepared structures, indicating the suitability of this approach to achieve nanostructures with low aggregation and subsequently higher surface area for an efficient reaction.

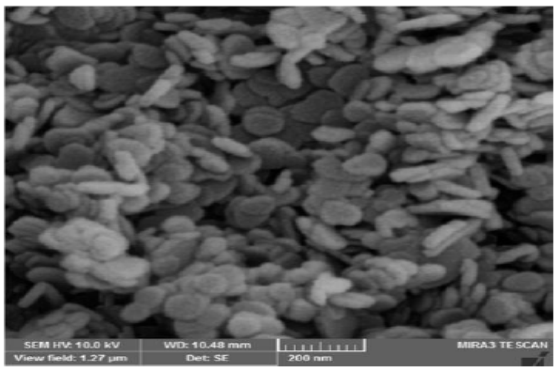


Figure 1. SEM image of MgO nanostructures.

B. CCD modeling

The experimental runs were performed according to the conditions represented in Table 2. Then the results were recorded as experimental removal efficiency. Based on the applied CCD model, an empirical mutual relationship between the response (amoxicillin removal efficiency (%)) and independent parameters was obtained as below:

Y (amoxicillin removal (%)) = 35.64 – 17.00 x1 + 7.65 x2 + 5.99 x3 – 3.04 x1x2 – 1.7 x1x3 + 0.55 x2x3 + 8.94 – 1.33 – 0.13 (3)

According to the above equation, the predicted values for amoxicillin removal efficiency during the process were calculated and written in Table 2.

Table 2. Experimental and predicted efficiencies for the adsorption of amoxicillin onto MgO nanostructures

Run	Amoxicillin conc. (mg /L)	Elapsed time (min)	MgO dosage (g/L)	Removal efficiency (%)		
				Experimental	Predicted	Residuals
1	7.00	50.00	0.50	20.35	25.94	5.59
2	4.62	73.78	2.09	79.54	79.28	-0.26
3	7.00	50.00	1.50	33.07	35.64	2.57
4	7.00	90.00	1.50	43.93	44.74	0.81
5	4.62	26.22	0.91	46.77	42.61	-4.16
6	7.00	50.00	1.50	37.12	35.64	-1.48
7	7.00	50.00	1.50	35.66	35.64	-0.02
8	4.62	73.78	0.91	64.69	62.92	-1.77
9	9.38	26.22	2.09	26.93	25.48	-1.45
10	9.38	73.78	0.91	29.05	26.19	-2.86
11	3.00	50.00	1.50	87.13	89.53	2.40
12	7.00	50.00	1.50	38.96	35.64	-3.32
13	4.62	26.22	2.09	57.21	56.80	-0.41
14	11.00	50.00	1.50	30.11	32.35	2.24
15	9.38	73.78	2.09	34.87	35.78	0.91
16	7.00	50.00	1.50	34.41	35.64	1.23
17	7.00	10.00	1.50	15.17	19.00	3.83
18	9.38	26.22	0.91	21.1	18.07	-3.03
19	7.00	50.00	2.50	47.04	46.09	-0.95
20	7.00	50.00	1.50	35.43	35.64	0.21

The suitability and significance of modeling process was evaluated using analysis of variance (ANOVA). The results of ANOVA are shown in Table 3.

Table 3. Analysis of variance (ANOVA) for amoxicillin removal by MgO nanostructures

Source of variations	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Regression	6565.38	9	729.49	59.90	0.0001
Residuals	121.79	10	12.18		
Lack of Fit	100.52	5	20.10	4.73	0.0567
Pure Error	21.27	5	4.25		
Total	6687.17	19			

R^2 = 0.982, adjusted R^2 = 0.965, Predicted R^2=0.881, Adequate precision = 28.97 and coefficient of variation (CV) = 8.53%.

The results provided in Table 3 showed the high coefficient of determination (R2=0.982), implying that 98.2% of the variations in the removal efficiency of amoxicillin can be described by the model and the

applied model fails to explain only 1.8 % of the variations [9]. To assess suitability of the model, experimental and predicted removal efficiencies were compared (Figure 2). Figure 2 demonstrated good agreement between the predicted and the experimental amoxicillin removal efficiency. It seems there is no significant difference between R2 (0.982) and adjusted R2 (0.965). The predicted R2 of 0.881 is in reasonable agreement with the adjusted R2 of 0.965. In addition, the F-value of 59.90 implies that the model is significant. The P-value, as a tool to check the significance of CCD, was less than 0.05, demonstrating the significance of the model terms [1]. It is important to note that "Adequate precision" measures the difference between the signal and the noise, and a ratio of greater than 4 is favorable [8]. Therefore, the obtained adequate precision of 28.97, which was obtained in the present study, indicated an adequate signal. In addition, a very low value of CV (8.53%) suggested the good reliability of the model [10].

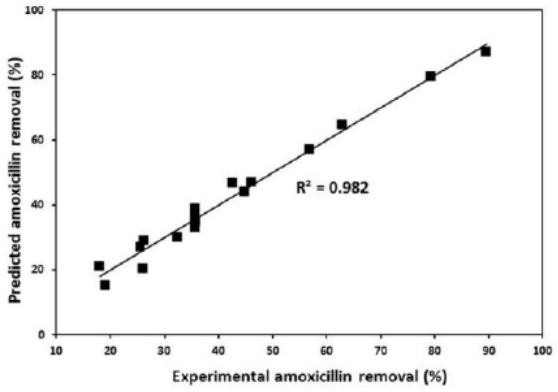


Figure 2. Plot of the predicted amoxicillin removal efficiencies versus corresponding experimental removal efficiencies

C. Effect of operational parameters

Three-dimensional (3-D) surface plots were used to evaluate the interaction between the dependent operational parameters and the response (amoxicillin removal (%)). As shown in Figure 3 (a), amoxicillin removal efficiency increased with increasing reaction time and decreasing the concentration of amoxicillin. Decreasing amoxicillin removal (%) with increasing its initial concentration can be attributed to higher adsorbate to adsorbent ratio, causing the saturation of adsorptive sites. This leads to decreasing the removal efficiency of amoxicillin at higher concentrations [11]. This plot was depicted based on MgO nanostructures dosage of 1.5 g/L. Fig. 3 (b) shows the effect of MgO dosage and the elapsed time on the removal of amoxicillin at an initial amoxicillin concentration of 7 mg/L. As

plotted, increasing MgO nanostructures dosage led to the increase in removal of amoxicillin. This is due to the increased number of available adsorptive sites with increasing adsorbent dosage, leading to the higher adsorption efficiency [12].

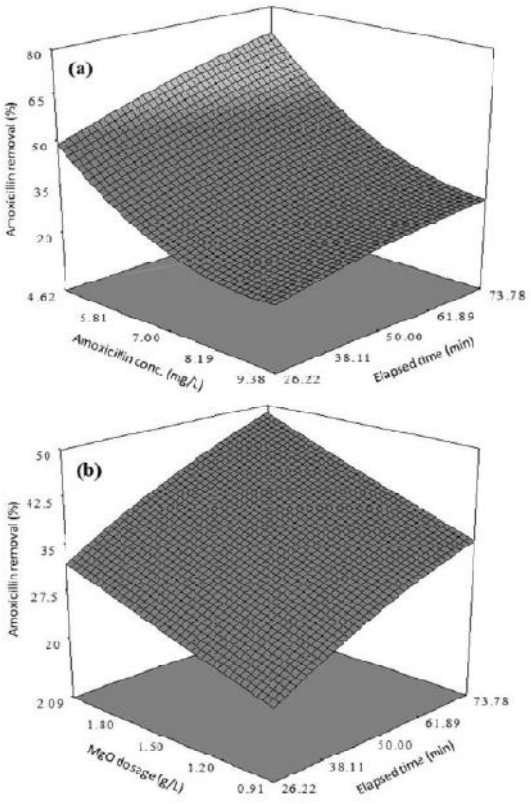


Figure 3. Three-D plots for amoxicillin removal (%) as the function of amoxicillin concentration (a) and MgO dosage (b).

D. Optimization of operational parameters

Numerical optimization was performed to specify optimum conditions to reach the maximum amoxicillin removal through the adsorption by MgO nanostructures. In this method, the response (amoxicillin removal) was set to the maximum level, while the other operational parameters were set to "in range" status in Design-Expert software. According to this approach, optimum conditions, which led to the maximum amoxicillin removal of 79.32%, included amoxicillin concentration of 4.62 mg/L, reaction time of 73.78 min and MgO nanostructures dosage of 2.09 g/L. To confirm the results of optimization, three additional experiments were carried out under optimized conditions. The results of this set of experiments showed an average amoxicillin removal of 80.04%, which confirmed the numerical optimization data.

CONCLUSIONS

A simple sonochemical method was used for the synthesis of MgO nanostructures. As-prepared nanostructures were used as an adsorbent for decontamination of amoxicillin-contained aqueous solutions. SEM image of the nanostructures confirmed excellent morphology of the sample with size distribution of lower than 100 nm. The process of

amoxicillin adsorption was response surface methodologically optimized. The results of analysis of variance (ANOVA) indicated a good correlation between experimental amoxicillin removal and predicted values estimated through the modeling (R2=0.982). The results of numerical optimization were checked by some confirmatory experiments under optimized operational parameters. Overall, the sonochemical method can be proposed as a suitable approach for the preparation of MgO nanostructures to be used as an effective adsorbent for removing low concentrations of amoxicillin from the liquid phase.

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