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Application of fuzzy modeling and response surface methodology for optimization of cadmium uptake by *Colpomenia sinosa*

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ABSTRACT

The optimum conditions for the removal of cadmium as heavy and toxic metals via a biomass were investigated in this program. The biomass was prepared from an eco-friendly, native, and low-cost algae microorganism, e.g., *Colpomenia sinuosa*. The cadmium uptake involved the biosorption process onto the cell wall of the Colpomenia sinuosa. The experiments were carried out on the five different parameters of temperature, algae biomass dosage, the initial cadmium concentration, pH of the cadmium solution, and contact time for interval times of cadmium of the biomass surface. The design of the experiment (DOE) was done for different conditions. The optimum conditions were compared via two optimization methods. Both the response surface methodology (RSM) and fuzzy modeling were treated with experimental data. The contour maps were planned for understanding the effects of two interactive factors. The combined effects of pH-temperature, pH-contact time, and algae biomass dosage-temperature were plotted for cadmium uptake.

1. Introduction

The biosorption process is defined as the removal of pollution from the environment using living systems in vitro or in vivo. Among the living systems, algae is a reasonable candidate as a microorganism with highly efficient biomass agents for pollution uptake onto its cell walls, an abundant population between plants, and it is possible to grow in all places. Therefore, it is a prime candidate as an economical, clean, reusable, eco-friendly, and available biomass. *Colpomenia sinuosa* is a brown algae species of the genus *Colpomenia* that is collected from the Persian Gulf. It is comprised of 11.3% carbohydrate, 9% protein content, and 3.1% total fat; the carbohydrate part includes the C6-C4-C6 phenolic compound as a biologically active secondary metabolite [1,2]. This study focused on 20 years of publications, journals, and books from the Science Direct website. The results showed about 7946 and 2288 publications for biosorption and biosorption of cadmium, respectively. A comparison of these results is shown in Figure

The results showed that a quarter of all publications about biosorption was related to the biosorption of cadmium. These statistical results were brought about by the significant research regarding the biosorption of cadmium. Although cadmium biosorption has been studied widely [3] and recently [4,5], no study has focused on a comparison of optimum conditions by response surface methodology and fuzzy modeling onto cadmium uptake by *Colpomenia.*

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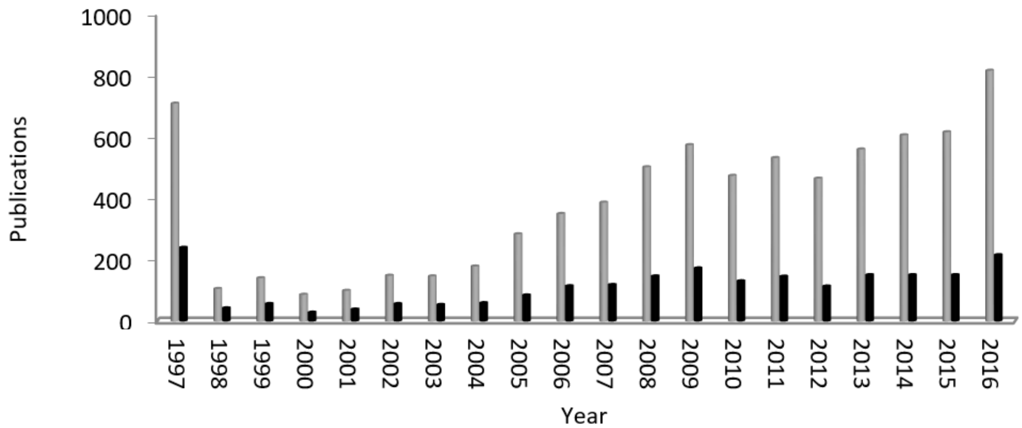

Fig. 1. The distribution of publications about biosorption (gray) and biosorption of cadmium (black) from 1997-2016

2. Material and methods

The *Colpomenia* was collected from the Bushehr area of the Persian Gulf. The algae was washed many times with distilled water, and used to prepare the biomass; it was dried in an oven at 60 °C for 24 hours. The microscale biomass was obtained by filtration [3]. The stock solution of Cd(II) was prepared from $Cd(NO_3)_2.4H_2O$, which was obtained from the Merck Co., Germany. Different initial pH was adjusted by HCl (0.1N) and NaOH (0.1N) solutions. The initial and equilibrium Cd(II) concentration (C_i and C_e) were found by an atomic absorption spectrometer (contrAA300 from Analytic Jena Co., Germany). For a given w (g) of the biomass and V (mL) of the solution, the equilibrium adsorption of Cd(II) onto biomass, q_e (mg/g), is calculated from the following equation:

$$q_e = \frac{(C_i - C_e)V}{1000w} \qquad (1)$$

3. Results and discussion

3.1. Response surface methodology (RSM)

Five parameters comprising pH (X_1), temperature (X_2), algae biomass dosage (X_3), Cd (II) concentration (X_4) and contact time (X_5) were adjusted by RSM [6]. The independent parameters are presented by Equation (2),

$$x_i = X_i - X_0 / \Delta x \qquad (2)$$

where X_i is the dimensionless coded value of the ith independent parameter, X_0 is the value of X_i at the center point, and Δx is the phase change value. Each parameter was arranged in 5 grades (-2, -1, 0, +1 and +2) and are specified in Table 1.

Table 1. The experimental parameters

Independent parameter	Range and levels				
	-2	**-1**	**0**	**1**	**2**
pH (X_1)	1	2	3	4	5
Temperature (X_2) °C	20	30	40	50	60
Algae biomass dosage (X_3) g/L	3	4	5	6	7
Cd (II) concentration (X_4) mg/L	50	75	100	125	150
Contact time (X_5) min	15	30	45	60	75

According to the polynomial Equation (3), the RSM can be developed and solved in Minitab software:

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \qquad (3)$$

where Y is the expected value, $X_i, X_j, \ldots, X_k$ are the singular effects, $X_i^2, X_j^2, \ldots, X_k^2$ are the square effects, X_iX_j, X_iX_k, X_jX_k are the interface effects, β_0 is the intercept, β_i (i=1, 2, . . . , k) is the coefficient of singular effects, β_{ii} (i=1, 2, . . . , k) is the coefficient of the squared effects and β_{ij} (i=1, 2, . . . , k, j=1, 2, . . . , k) is the coefficient of the interaction effects [7]. From the preliminary lists in the experimental designing, 32 trials were selected to obtain the observed data. Next, the theoretical cadmium uptake was obtained for the best situations by Equation (4).

$$Y=71.2347-0.0719X_1+1.1815X_2+0.5031X_3+1.1034X_4+1.0035X_5+0.6873X_1^2-0.3099X_2^2+1.1313X_3^2-0.9112X_4^2-0.0002X_5^2+0.6039X_1\times X_2+0.0847X_1\times X_3+0.7910X_1\times X_4-0.0625X_1\times X_5-1.7630X_2\times X_3-0.8174X_2\times X_4-1.4541X_2\times X_5+0.6338X_3\times X_4-2.4560X_3\times X_5-0.4097X_4\times X_5 \qquad (4)$$

Table 2. Analysis of variance for response surface methodology

R-Sq =97.61%, R-Sq(adj) =93.27%

Term	Coef	SE Coef	T	P
Constant	71.2347	0.3734	190.791	0.000
X_1	-0.0719	0.1911	-0.376	0.714
X_2	1.1815	0.1911	6.183	0.000
X_3	0.5031	0.1911	2.633	0.023
X_4	1.1034	0.1911	5.775	0.000
X_5	1.0035	0.1911	5.252	0.000
X_1*X_1	0.6873	0.1728	3.977	0.002
X_2*X_2	-0.3099	0.1728	-1.793	0.100
X_3*X_3	1.1313	0.1728	6.546	0.000
X_4*X_4	-0.9112	0.1728	-5.272	0.000
X_5*X_5	0.0002	0.1728	-0.001	0.999
X_1*X_2	0.6039	0.2340	2.581	0.026
X_1*X_3	0.0847	0.2340	0.362	0.724
X_1*X_4	0.7910	0.2340	3.380	0.006
X_1*X_5	-0.0625	0.2340	-0.267	0.794
X_2*X_3	-1.7630	0.2340	-7.534	0.000
X_2*X_4	-0.8174	0.2340	-3.493	0.005
X_2*X_5	-1.4541	0.2340	-6.214	0.000
X_3*X_4	0.6338	0.2340	2.708	0.020
X_3*X_5	-2.4560	0.2340	-10.495	0.000
X_4*X_5	-0.4097	0.2340	-1.751	0.108

The simplified Equation (5) was obtained from the extended Equation (4) through statistical methods (t-test and p-values) as shown in Table 2 at the 95% confidence level [8].

$$Y=71.2347+1.1815X_2+0.5031X_3+1.1034X_4+1.0035X_5+0.6873X_1^2+1.1313X_3^2-0.9112X_4^2+0.6039X_1\times X_2+0.7910X_1\times X_4-1.7630X_2\times X_3-0.8174X_2\times X_4-1.4541X_2\times X_5+0.6338X_3\times X_4-2.4560X_3\times X_5 \quad (5)$$

The correlation coefficient R^2 (97.61%) and the adjusted R^2(93.27%) were supported by model [9]. The maximum Cd(II) uptake of 86.5% was achieved for 150 mg/L (initial Cd(II) concentration), 7 g/L (adsorbent dose), 75 minute (contact time), 20°C, and pH=5.00 [10,11].

3.2. Fuzzy logic

Each fuzzy consists of three platforms: fuzzification, inference engine, and defuzzification [12]. The experimental data are categorized in three levels, namely high, medium, and low. 2 and 1 (for RSM) are represented High (for fuzzy), 0 (for RSM) is represented Medium (for fuzzy) and finally -2 and -1 (for RSM) are represented Low (for fuzzy) as shown in Table 1. [13,14]. A fuzzy number describes the correlation between x and a membership function *f*(x), which ranges between 0 and 1 [15,16].The membership function of the input parameters and a graphical representation of the fuzzy logic is displayed in Figure 2.

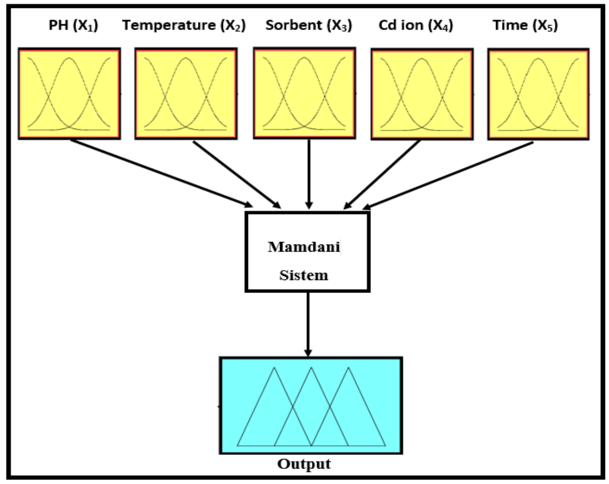

Fig. 2. The input parameters in fuzzy modeling

For each input parameters, both equations (6) and (7), as triangle membership functions (MFs), are established [17-19]

$$(x, a, b, c) = \begin{cases} 0 & x \le a \\ & \text{or} \\ & x \ge c \\ \frac{x-a}{b-c} & a \le x \le b \\ \frac{c-x}{c-b} & b \le x \le c \end{cases} \quad (6)$$

$$f(x, a, b, c) = \max\left(\min\left(\frac{x-a}{b-c}, \frac{c-x}{c-b}\right), 0\right) \quad (7)$$

The parameters *a* and *c* locate the “bottoms” of the triangle, and the parameter *b* locates the “top” [12,20].

Each rule in the Mamdani model is represented by an IF-THEN relationship. The fuzzy systems translate these rules into their mathematical matches. Eleven rules were used for the fuzzy sets, which are shown in Table 3 and Figure 3.

Table 3. Eleven IF-THEN relationships rules in the Mamdani model

			IF			And
Rul	**pH**	**tempera**	**sorb**	**Cd (II)**	**cont**	**%**
1	high	low	high	high	high	high
2	medi	high	low	low	low	low
3	low	medium	medi	medium	low	medi
4	low	medium	medi	medium	medi	medi
5	medi	medium	low	medium	low	low
6	high	low	low	medium	medi	high
7	high	low	low	low	low	high
8	high	low	medi	medium	medi	high
9	medi	high	low	low	high	low
10	high	low	high	low	high	high
11	low	medium	low	low	medi	medi

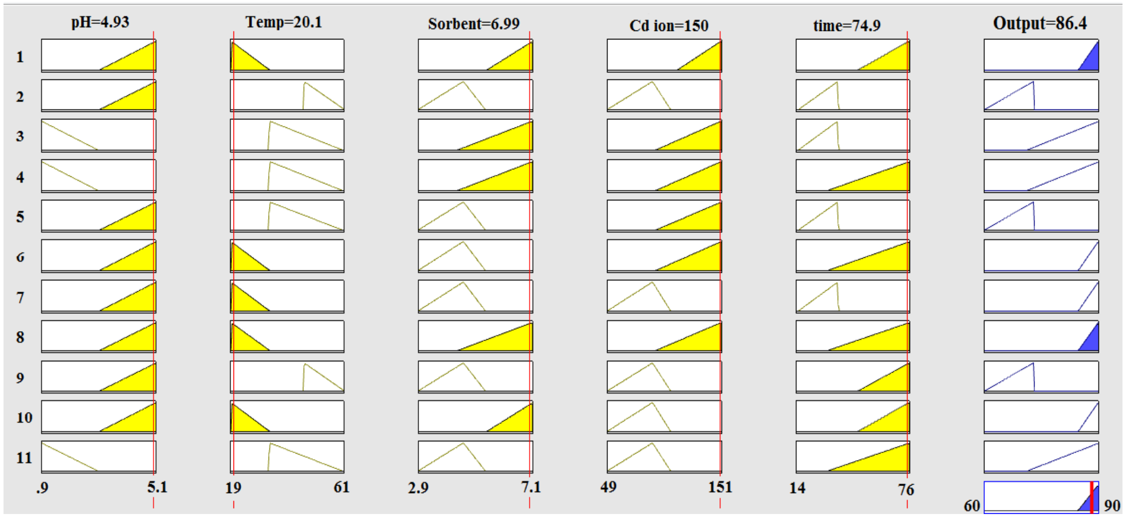

Fig. 3. The inputs and outputs investigating for eleven rules

All the rules would be inferred, and the results of the inferences of individual rules collected. According to fuzzy modeling, the optimum conditions were set as 150 mg/L (initial Cd(II) concentration), 20.1°C, pH=4.93, 6.99 g/L (adsorbent dose), and 74.9 minute (contact time). At these conditions, the maximum Cd(II) uptake was found to be 86.4 % [17-19], [21].

3.3. The Counter maps

The response surface plots and contour maps describe changing two factors while maintaining all other factors at a fixed level, simultaneously. Both strategies deliberate the foremost and collaboration effects of two interactive factors [22,23]. Figure 4 shows an interactive effect of pH and temperature on the Cd(II) uptake at a constant 7 g/L (algae biomass dosage), 45 minutes (contact time), and 100 mg/L (initial cadmium concentration). The Cd(II) uptake is low-grade at higher temperatures (20 to 60˚C). The high temperature caused the widespread interruption of the cell wall of the Colpomenia sinuosa algae, and therefore a decrease in Cd(II) uptake [24-27].

Figure 5 shows an interactive effect of pH and contact time on the Cd(II) uptake at 45˚C, 100 mg/L (initial cadmium concentration), and 5g/L (algae biomass dosage). The Cd(II) uptake is 78.51% in 75 minutes and a pH=5.

Figure 6 shows the interactive effect of the algae biomass dosage and temperature on Cd(II) uptake at 45 minutes (constant contact time), 100 mg/L (initial cadmium concentration), and initial pH=3. The sharp increase in the Cd(II) uptake occurred when the algae biomass dosage changed from 5 g/L to 7 g/L. The Cd(II) uptake is 84.7% at an algae biomass dosage of 7g/L and a temperature of 20˚C.

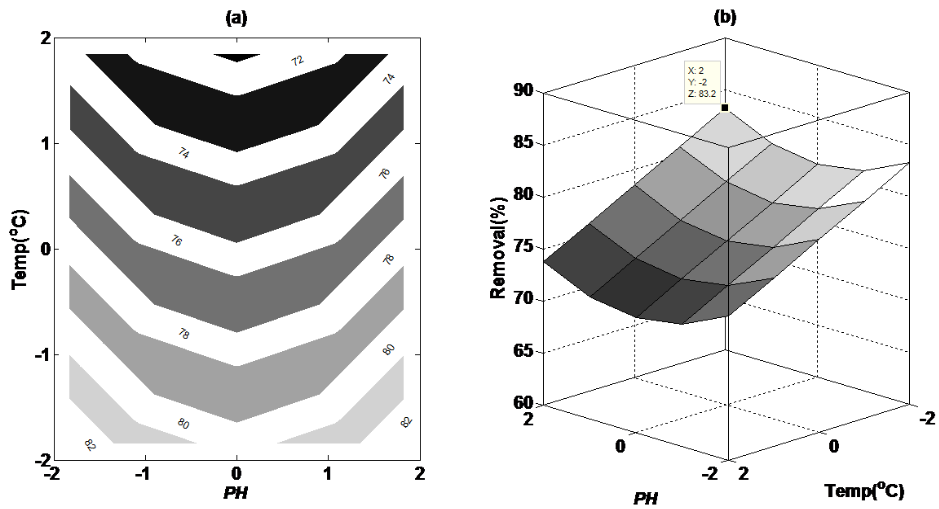

Fig.4. The combined effects between pH and temperature on Cd(II) uptake: (a) Contour plot and (b) Response surface plot

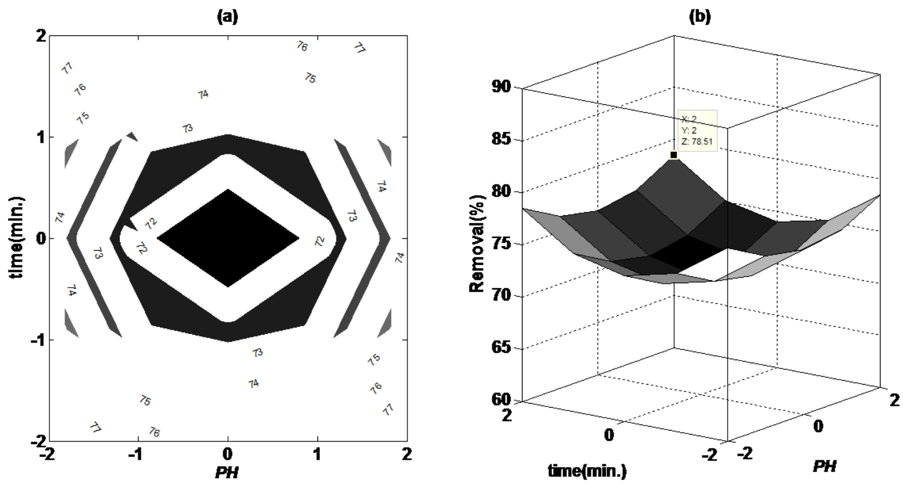

Fig. 5. The combined effects between pH and contact time on Cd(II) uptake: (a) Contour plot and (b) Response surface plot

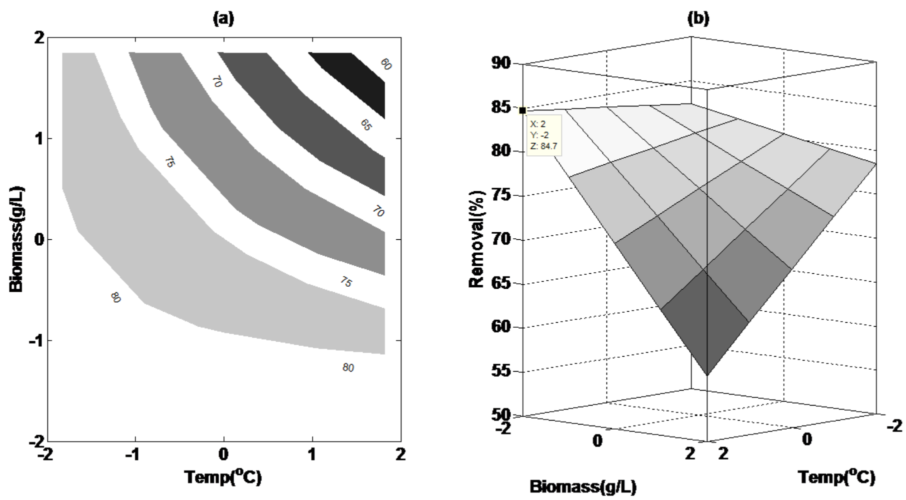

Fig. 6. The combined effects between algae biomass dosage and temperature on Cd(II) uptake: (a) Contour plot and (b) Response surface plot

3.4. The comparison of response surface methodology with fuzzy modeling

The matching of RSM and fuzzy modeling versus the experimental data on the removal of Cd(II) using *Colpomenia* is shown in Figure 7. The results indicated that the correlation coefficient, R^2, was equal to 97.61 and 96.74 for RSM and fuzzy modeling, respectively. The results of both simulations (RSM and fuzzy modeling) showed good agreement with the experimental data [17-19], [21].

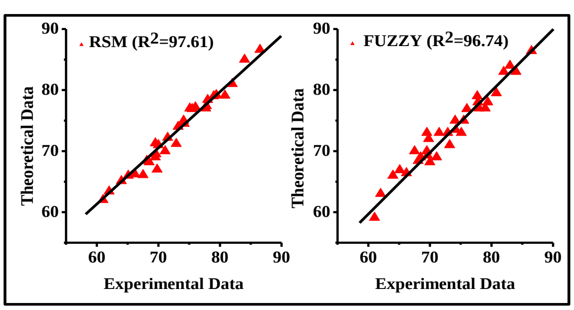

Fig. 7. The comparison of RSM and fuzzy models

Conclusions

The optimum conditions were established for both response surface methodology and fuzzy modeling. The maximum of the Cd(II) uptake based on RSM and fuzzy model were 84.7% and 86.4%, respectively. The best condition for the maximum uptake was equal to temperatures of 20 ˚C, a time of 75 minutes, a pH=5, a biomass dosage of 7 g/L, and a Cd (II) concentration of 150 mg/L. The R2 for RSM and Fuzzy were 97.61 and 96.47, respectively. The comparison of the RSM and fuzzy modeling versus the experimental data showed good agreement with the experimental data.

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