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Studies on biosorption of cadmium on grape pomace using response surface methodology

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ABSTRACT

In this study, a new biosorbent material, juice industry waste grape pomace was used as an adsorbent. Studies on the removal of cadmium from aqueous solutions using grape pomace were undertaken. The experiments were designed by full factorial design method (3–1 fractional factorial design). The fit of the model was checked by the determination coefficient (R^2). In this case the value of the determination coefficient was 0.99916 indicates that only 0.00004% of the total variation was not explained by the model. The value of the adjusted determination coefficient 0.999 was also high significance of the model. The points giving the maximum removal efficiency of Cd(II) were found to be pH 5.2 and powdered grape pomace 12.5 g/L, temperature was 28.5°C, and the initial (aqueous) metal concentration was 43 mg/L.

Keywords: Biosorption; Cadmium removal; Grape pomace; Full factorial experimental design

1. Introduction

Heavy metals are toxic and non-biodegradable pollutants released into the environment by industrial, mining and agricultural activities [1]. The conventional treatments used to remove heavy metals from waste waters are precipitation, coagulation, reduction and membrane processes, ion-exchange and adsorption. However, the application of such processes is often restricted because of technical and/or economic constraints. For example, the precipitation processes cannot guarantee the metal concentration limits required by regulatory standards and produce wastes difficult to treat; on the other hand, ion-exchange and adsorption processes are very effective but require expensive adsorbent materials and difficult plant management [2].

In this general setting, the search for a new economical and effective heavy metal adsorbent focuses on biomaterials such as bacterial and algal biomasses [3]. The advantages of biosorption lie in both the good performance and metal removal, often comparable with their commercial competitors (ion-exchangers) and cost-effectiveness; making use of algae and raw materials of fermentation and agricultural processes

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[4]. Different forms of non-living plant materials such as rice husk [5], sawdust [6] and cone biomass [7] have been widely investigated as potential biosorbents.

Cadmium is one of the toxic metal, which is widely used in industrial processes. The discharge of effluents from many industries is the main source of cadmium contamination on aquatic and terrestrial environment [8,9]. Its highly toxic effects to humans have been well documented [10,11]. Factorial design employed avoiding the traditional one factor at a time experiments. Common statistical tools, such as analysis of variants, F-test, the Student's t-test and lack of fit, were used to define the most important process variables affecting the metal removal efficiency [12]. The factorial experimental design methodology involves changing all the variables from one experiment to the next. The reason for this is that variables can influence each other, and the ideal value for one of them can depend on the values of the others. This interaction between variables is a frequent phenomenon [12]. Many studies concerning the uptake of heavy metals have indicated that temperature [14,15] and pH [13,14–20] influence removal efficiency. However, few employ the factorial design method for evaluating the influence of the operation variables on these processes [19,21].

Agriculture, forestry, and fisheries have been generating large quantities of various biomass wastes and some of them contain various natural materials with interesting functional groups, such as carboxyl, hydroxy, amidocyanogen and so on. Grape pomace is one of the valuable biomass wastes. In this study, a new biosorbent material, juice industry waste grape pomace was used as an adsorbent. Till now, there is no relevant work reported on the grape biomass for removal of Cd(II) and it is a promising novel biosorbents.

2. Experimental

2.1. Preparation of adsorbent

The juice industry waste, grape pomace was collected from local shops and washed thoroughly with demineralized water. The crude grape residue was dried in a convection oven at 80–100˚C for 48 h. The dried residue was ground in a conventional mixer grinder. The powder was washed with de-ionized water and subjected to vacuum filtration. The filter cake was collected and redissolved in de-ionized water and left for sedimentation. The sediment was collected and ground to powder such that it passes through a 100 sieve mesh.

2.2. Preparation and analysis of Cd^{2+} ions

The stock solution (1,000 mg/l) of Cd^{2+} was prepared by dissolving required amount of $CdCl_2$ $2H_2O$ in demineralized water. Concentrations ranging from 12 to 60 mg/l were prepared by appropriate dilution of above stock solution. The concentration of Cd^{2+} ions in samples were determined by using Atomic Absorption Spectrophotometer Analyst AA200 (Perkin Elmer make).

2.3. Biosorption studies

Batch studies were conducted in 250 ml Erlenmeyer flasks to elucidate the best operating conditions, which enhance Cd^{2+} adsorption. The flaks containing solution and grape pomace were shaken for the required amount of time and the pH of solution (3–7) was adjusted by using 0.1 N HCl and 0.1 N NaOH. The initial concentrations of Cd^{2+} ions were varied from 12 to 60 mg/l (12, 24, 36, 48, 60 mg/l). Different amounts of biomass ranging from 0.5 to 2.5 g were contacted with 100 ml Cd^{2+} solution. The adsorption capacity C_S was calculated.

2.4. Effect of time

Fig. 1 shows the variation of aqueous metal concentration with time. It can be observed that the aqueous metal concentration decreases with increase in time and reaches platue-indicating attainment of equilibrium in 1½ hours. Hence all the batch experiments for a period of more than 1½ hours in order to ascertain the attainment of equilibrium.

3. Statistical design of experiments

Factorial design is employed to reduce the total number of experiments in order to achieve optimiza-

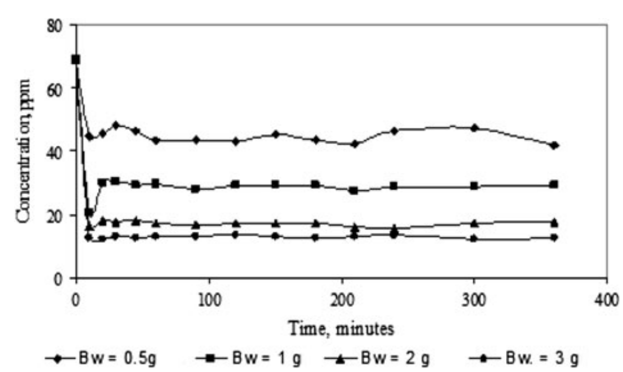

Fig. 1. Variation of cadmium concentration with time at different biomass weights.

tion of the system [22–24]. The factorial 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 (Table 1).

Effects are differential quantities expressing how a response changes as the levels of one or more factors are changed [22,23]. Also, factorial designs allow measuring the interaction between each different group of factors.

Interactions are the driving force in many optimizations of processes. Without the use of factorial experiments, important interactions may remain undetected and the overall optimization may not be attained [22,23]. One of the simplest types of factorial designs used in experimental work is one having two levels (2^k) [22–24]. In a full factorial experiment, responses are measured at all combinations of the experimental factor levels. The combination of factor levels represents the conditions at which responses will be measured. In the investigation of Cadmium removal using grape pomace from aqueous solution could depend on initial concentration of metal ion, the acidity of the aqueous solution, temperature and weight of the biomass. Other variables such as speed of shaker 160 rpm, volume of the aqueous solution 100 ml were kept constant.

The factor levels were coded as −2 (low), −1, 0 (central), 1 and 2 (high). For the analysis of data Statistica version 6.0 was employed. The effect of the variables and their interactions were measured by performing a set of 26 experiments containing two central points, in order to evaluate the standard deviation of each factor and to detect if there is any inflection point [25,26] forming the 2^4 full factorial designs given in Fig. 2.

4. Results and discussions

In this work the factors screened were initial metal concentration, pH, biomass weight and temperature. The experiments given in Tables 1 and 2 were carried out and solid metal loading was estimated. The software package Statistica version 6.0 was employed in order to obtain the effect of these variables.

The regression analysis was performed to fit the response function to the experimental data. The result of the analysis was given in Table 3. Variables giving quadratic and interaction terms with the largest absolute coefficients in the fitted models were chosen for the axes of the response surface plots to account for curvature of the surfaces. The significance of each coefficient was determined by t-test and p-values which are listed in the table. The larger the magnitude of t-value and smaller the p-value, more significant in the corresponding coefficient [27].

This implies first-order main effects of initial metal concentration, pH and biomass bead volume are more significant than their quadratic main effects. The statistical significance of second-order model equation was evaluated by the analysis of variance which revealed that the regression was statistically at 95% confidence level. The fit of the model was checked by the determination of R^2 value and in present case which is equal to 0.99961 indicating that only 0.04% of the total variation was not explained by the model. The value of the adjusted determination coefficient (Adjus. R^2 0.99911) is also high showing the high significance of the model [28].

The response surface to estimate the uptake efficiency of Cd^{+2} over independent variables pH, initial metal Concentration is depicted in Fig. 2. The points giving the maximum uptake of Cd^{++} were found to be at a pH of 5.2. Increase in pH resulted in an increase in Cd^{+2} uptake till to 5.2 and further increasing the pH resulting decreased the metal uptake. The poor sorption of Cd^{+2} in the low pH range could have been due to competition with the H^+ ions for metal-binding sites on the biomass cells, while the increase in pH favors metal sorption mainly because of negatively charged groups [29–31]. Further, it was observed that the weight of the biomass was 1.125 g optimized. Either decreasing or increasing (Fig. 3) the

Table 1
Experimental range and levels of independent variables

Level	BW (g)	Metal conc. (mg/L)	pH	Temperature (°C)
−2 (low level)	0.5	12	3	10
−1	1	24	4	20
0 (central)	1.5	36	5	30
1	2	48	6	40
2 (high level)	2.5	60	7	50
ΔS (step change)	0.5	12	1	10

Table 2
Full factorial design containing two central points

Run	BW	Metal conc.	pH	Temp.	C_S
1	−1.0000	−1.0000	−1.0000	−1.0000	2.1800
2	−1.0000	−1.0000	−1.0000	1.0000	2.1300
3	−1.0000	−1.0000	1.0000	−1.0000	2.2680
4	−1.0000	−1.0000	1.0000	1.0000	2.1000
5	−1.0000	1.0000	−1.0000	−1.0000	3.6500
6	−1.0000	1.0000	−1.0000	1.0000	3.6000
7	−1.0000	1.0000	1.0000	−1.0000	3.6400
8	−1.0000	1.0000	1.0000	1.0000	3.6000
9	1.0000	−1.0000	−1.0000	−1.0000	1.0616
10	1.0000	−1.0000	−1.0000	1.0000	0.9466
11	1.0000	−1.0000	1.0000	−1.0000	1.0800
12	1.0000	−1.0000	1.0000	1.0000	1.0200
13	1.0000	1.0000	−1.0000	−1.0000	2.1033
14	1.0000	1.0000	−1.0000	1.0000	1.9983
15	1.0000	1.0000	1.0000	−1.0000	2.0566
16	1.0000	1.0000	1.0000	1.0000	2.0066
17	−2.0000	0.0000	0.0000	0.0000	4.3616
18	2.0000	0.0000	0.0000	0.0000	1.5950
19	0.0000	−2.0000	0.0000	0.0000	0.6966
20	0.0000	2.0000	0.0000	0.0000	3.1200
21	0.0000	0.0000	−2.0000	0.0000	1.9350
22	0.0000	0.0000	2.0000	0.0000	2.0316
23	0.0000	0.0000	0.0000	−2.0000	2.0833
24	0.0000	0.0000	0.0000	2.0000	1.9833
25 (C)	0.0000	0.0000	0.0000	0.0000	4.8900
26 (C)	0.0000	0.0000	0.0000	0.0000	4.9700

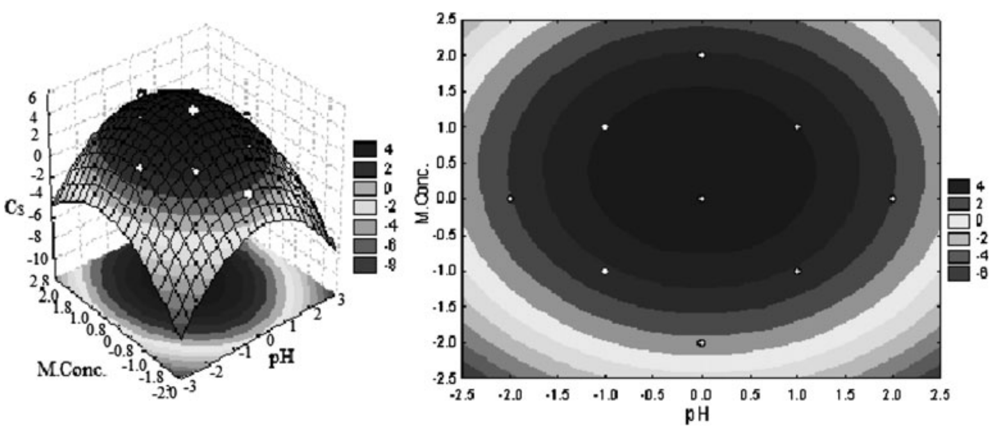

Fig. 2. Response surface plot for the pH and metal concentration.

biomass weight resulted that the decrease the metal adsorption.

The different initial metal concentrations were evaluated and observed that at initial metal concentration of 43 mg/L the adsorption was high. Further, it was observed that the optimized temperature (Fig. 4) for the adsorption of Cd^{+2} on grape pomace was at 28.5˚C. The significance of each coefficient was determined by t-test

Table 3
Main effects and interaction analysis of biomass weight, initial metal concentration, pH and temperature for removal of Cd(II)

	Regression	Standard error	$t(11)$	P	−95%	+95%
Mean/interc.	4.9300	0.0251	195.8736	0.0000	4.8746	4.9853
(1) B.W (L)	−0.6845	0.0072	−94.2091	0.0000	−0.7004	−0.6685
B.W (Q)	−0.4897	0.0085	−57.4785	0.0000	−0.5084	−0.4709
(2) M.Conc (L)	0.6131	0.0072	84.3876	0.0000	0.5971	0.6291
M.Conc (Q)	−0.7572	0.0085	−88.8758	0.0000	−0.7759	−0.7384
(3) pH (L)	0.0122	0.0072	1.6898	0.1191	−0.0037	0.0282
pH (Q)	−0.7384	0.0085	−86.6751	0.0000	−0.7572	−0.7197
(4) Temperature (L)	−0.0349	0.0072	−4.8057	0.0005	−0.0509	−0.0189
Temperature (Q)	−0.7259	0.0085	−85.2079	0.0000	−0.7447	−0.7072
1L by 2L	−0.1097	0.0088	−12.3286	0.0000	−0.1292	−0.0901
1L by 3L	0.00033	0.0088	0.0375	0.9707	−0.0192	0.0199
1L by 4L	−0.0013	0.0088	−0.1545	0.8800	−0.0209	0.0182
2L by 3L	−0.0123	0.0088	−1.3907	0.1918	−0.0319	0.0072
2L by 4L	0.0092	0.0088	1.0395	0.3208	−0.0103	0.0288
3L by 4L	0.0001	0.0088	0.0140	0.9890	−0.0194	0.0197

Effect estimates; Var.: C_s; $R^2 = 0.99961$; Adj: 0.99911.

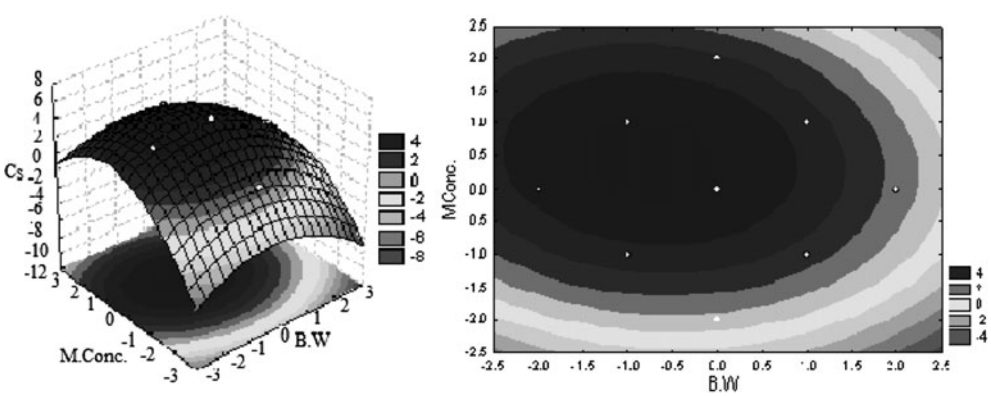

Fig. 3. Response surface plot for the metal concentration and biomass weight.

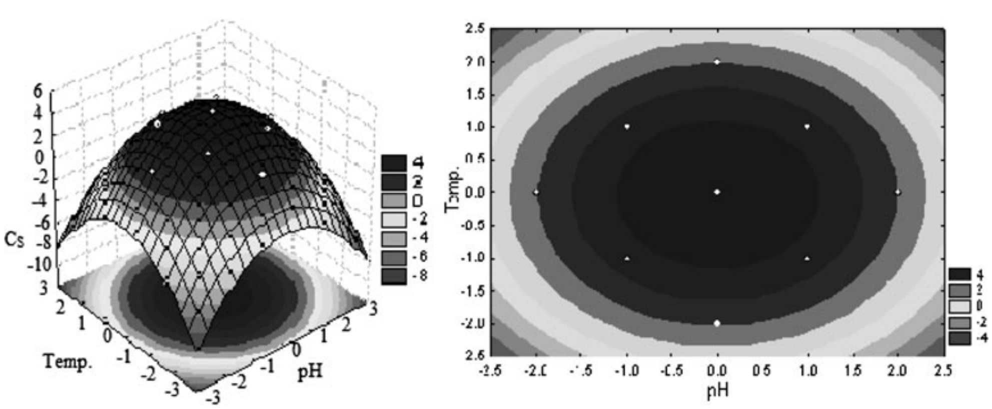

Fig. 4. Response surface plot for the pH and temperature.

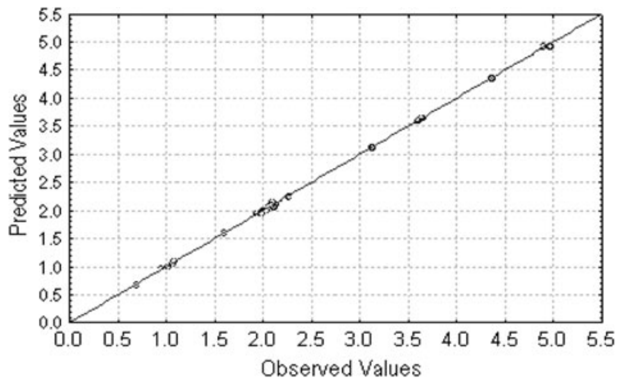

Fig. 5. Predicted and observed values with residual values.

and p-values, which are listed in the table. The larger the magnitude of t-value and smaller the p-value, more significant in the corresponding coefficient. The predicted and observed values were not much differentiation and it was observed that the same values were observed (Fig. 5).

$$\begin{aligned} C_S = {} & 4.93 - 0.6845X_1 - 0.489708X_1^2 + 0.6131X_2 \\ & - 0.757208X_2^2 + 0.0122X_3 - 0.7384X_3^2 \\ & - 0.03491X_4 - 0.7259X_4^2 - 0.1097X_1 \times X_2 \\ & + 0.0003X_1 \times X_3 - 0.0013X_1 \times X_4 \\ & - 0.0123X_2 \times X_3 + 0.00925X_2 \times X_4 \\ & + 0.0001X_3 \times X_4. \end{aligned}$$

where X_1 is Biomass weight, X_2 is Initial metal concentration, X_3 is pH, and X_4 is temperature. The above equation fits data well with an R^2 deviation of 0.99961. Figure shows the variation of predicted value with that of the observed value and it clearly shows that the fitness of the proposed equation is very good.

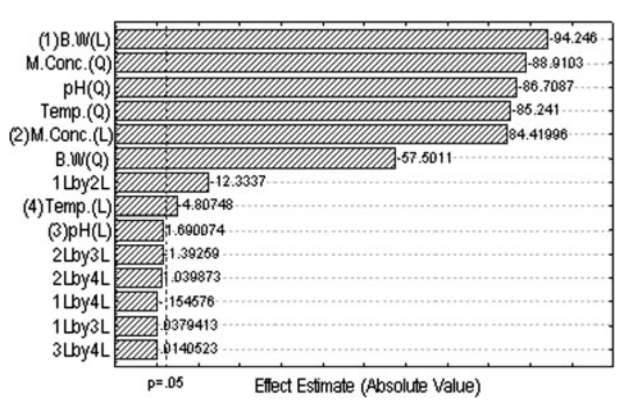

Fig. 6. Pareto chart of effects on the removal efficiency of Cd^{2+}.

The Pareto chart given in Fig. 6 it showed that the very significant.

5. Conclusions

The maximum removal efficiency of Cd(II) were found to be pH 5.2 and powdered grape pomace 12.5 g/L, temperature was 28.5°C and the initial (aqueous) metal concentration was 43 mg/L. Fitting of the model was checked by the determination coefficient (R^2), determination coefficient was 0.99916 indicated that only 0.00004 of the total variation was not explained by the model. The value of the adjusted determination coefficient 0.99911 was also high significance of the model. Hence, the grape pomace, juice industry waste is a promising novel biosorbents for the removal of Cd(II).

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Nomenclature

BW	—	biomass weight, g
C_0	—	initial metal ions concentration (mg/L)
C_S	—	concentration of metal ions in solid biomass (mg/g)
pH	—	negative logarithm of hydrogen ion concentration
Temp	—	temperature, °C

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