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Optimization with response surface methodology (RSM) of adsorption conditions of Cd(II) ions from aqueous solutions by pumice

Ponza ile sulu çözeltilerden Cd(II) iyonlarının adsorpsiyon koşullarının cevap yüzey yöntemi (CYY) ile optimizasyonu

Research Article

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ABSTRACT

Optimization of medium conditions for Cd(II) adsorption by pumice was studied through experimental designs. A multi step response surface methodology (RSM) including 2^{6-2} fractional factorial design (FFD), steepest ascent and central composite design (CCD) was successfully applied to optimize the adsorption conditions for Cd(II) ions from aqueous solutions. The most influential medium parameters were determined as pH, initial Cd(II) concentration and temperature via FFD. Then steepest ascent was used to determine the neighborhood region of the optimum point. Finally, CCD was applied to develop a response surface for optimization of adsorption conditions. The optimum conditions for Cd(II) adsorption were evaluated to be 7.01, 107.14 mg/L and 32.48°C for pH, initial Cd(II) concentration and temperature, respectively. A quadratic model was developed by CCD to represent Cd(II) ions adsorption.

Key Words
Adsorption, central composite design, pumice, response surface methodology

ÖZET

Ponza ile Cd(II) adsorpsiyonu için ortam koşullarının optimizasyonu deneysel tasarım ile çalışılmıştır. 2^{6-2} Fraksiyonel faktoriyel tasarım (FFD), en yüksek artış ve merkezi kompozit tasarımı (MKT) içeren çok basamaklı bir cevap yüzey yöntemi (CYY), sulu çözeltilerden Cd(II) iyonlarının adsorpsiyon koşullarını optimize etmek için başarılı bir şekilde uygulanmıştır. En etkili ortam parametreleri FFD ile pH, başlangıç Cd(II) derişimi ve sıcaklık olarak belirlenmiştir. Daha sonra optimum noktaya yakın aralıkların belirlenmesi için en dik artış yöntemi uygulanmıştır. Son olarak, adsorpsiyon koşullarının optimizasyonunda bir cevap yüzeyi geliştirmek için MKT uygulanmıştır. Cd(II) adsorpsiyonu için optimum koşullar pH, başlangıç Cd(II) derişimi ve sıcaklık için sırasıyla 7.01, 107.14 mg/L ve 32.48°C olarak belirlenmiştir. Cd(II) iyonlarının adsorpsiyonunu açıklamak için MKT ile bir kuadratik model geliştirilmiştir.

Anahtar Kelimeler
Adsorpsiyon, merkezi kompozit tasarımı, ponza taşı, cevap yüzey yöntemi

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INTRODUCTION

Wastewaters from industries such as plating, ceramics, glass, mining and battery manufacturing are considered the main sources of heavy metals, which cause the contamination of groundwaters with toxic metals. Especially, heavy metal pollution has raised serious environmental concerns worldwide because bioaccumulation of these elements beyond the tolerance thresholds of living organisms poses long-term risk to the earth's ecosystem and human health [1,2]. These heavy metals such as lead (Pb), chromium (Cr), copper (Cu), cadmium (Cd), nickel (Ni), and zinc (Zn) are toxic and have negative effects on environment and public health even exist at low concentrations [3]. It has been proved that metal ions such as Pb(II), Cd(II), Hg(II), Ni(II), Cu(II) can inhibit metabolic functions of aquatic life by specifically binding proteins and small metabolites in living cells, which cause severe health problems [4].

A wide range of methods including ion exchange, solvent extraction, reverse osmosis, precipitation, chemical oxidation and reduction, filtration, electrochemical treatment and adsorption are available for the removal of metal ions from aqueous solutions. However, all these conventional methods are rather expensive [5,6]. The adsorption process has been the most frequently applied method in the industries, and still is the most widely studied. A number of researchers have utilized wide variety of adsorbents to remove heavy metal ions from aqueous solutions [7-13]. However, new economic adsorbents, which are locally available and have high adsorption capacity, are still needed.

Cd was selected as a target heavy metal to be adsorbed by pumice for this study, because it is introduced in to bodies of water from smelting, metal plating, Cd-Ni batteries, phosphate fertilizer, mining, pigments, stabilizers, alloy industries and sewage sludge. The harmful effects of Cd include a number of acute and chronic disorders, such as "itai-itai" disease, renal damage, emphysema, hypertension, and testicular atrophy [14]. The drinking water guideline value recommended by World Health Organization [15], is 0.005 mg Cd/L. Low concentration (less than 5 mg/L) of Cd is difficult to treat economically using chemical precipitation methodologies. Pumice is a light, porous igneous volcanic rock produced by the release of gases during the solidification of lava [11] and it is a very common natural product. Pumice has high silica content (70.90% SiO_2) and it is mainly used in various industries such as cement production, watch, textile, agricultural, dental and chemical industries [16,11]

The aim of this study was to determine the course of Cd(II) sorption in the single-component system by pumice collected from the north of Van Lake, Turkey and optimize the most influential parameters on adsorption with RSM. The traditional methods using the one factor at a time method is extremely time consuming and expensive for a large number of parameters. To overcome this difficulty, some methods based on statistical have been used. Recently, RSM, a statistical method, has attracted great attention. RSM is a useful statistical technique for the investigation and optimization of experimental processes. RSM is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables [17].

MATERIALS AND METHODS

Adsorbent preparation

Pumice, which is used as an adsorbent, was collected from north of Lake Van, Turkey. Before used as adsorbent, pumice samples were washed with distilled water several times to remove impurities. Then, it was dried in a drying-oven at 250°C for 6 h. Subsequently, it was grounded with mill to obtain desired particle size. It was stored in a desiccator for further uses without any pretreatment. Table 1 represents the composition of utilized pumice by Energy-dispersive X-ray spectroscopy (EDX) analysis.

Cd(II) solutions

A stock solution of Cd(II) (1000 mg/L) was prepared by dissolving $Cd(NO_3)_2.4H_2O$ in 250 mL of distilled water. Necessary dilutions were made from the stock solution to prepare solutions in the range of desired concentrations. The initial pH of each solution was adjusted by 0.1 M HNO_3 and 0.1 M NaOH solutions before adsorption.

Batch adsorption experiments

Each experiment was carried out in 100 mL

Table 1. Composition of utilized pumice for the adsorption of Cd(II) ions.

Component	**Amount by percentage (%)**
Na_2O	2.610
MgO	0.216
Al_2O_3	11.700
SiO_2	74.090
P_2O_5	0.003
SO_3	0.098
Cl	0.052
K_2O	5.105
CaO	0.527
TiO_2	0.090
V_2O_5	0.006
Cr_2O_3	0.002
MnO	0.067
Fe_2O_3	1.455

erlenmeyer flasks containing 50 mL Cd(II) solution on temperature-controlled magnetic stirrer (adsorbent amount of fixed at 5 g). The concentrations of unadsorbed Cd(II) in filtrate solutions were determined using flame atomic absorption spectrophotometer (THERMO Solar AA Series spectrometer, USA) after the separation of adsorbent by filtration with whatman filter paper (No:42). The instrument response was periodically checked by standard metal solutions. The amount of adsorbed metal ions (Q_e) per gram of pumice was calculated using Eq. 1:

$$Q_e = \frac{(C_i - C_f)V}{m} \qquad (1)$$

Where Q_e is the amount of metal ions adsorbed onto pumice at equilibrium (mg Cd(II) ions/g pumice), C_i is the initial metal ion concentration in solution (mg/L), C_f is the final metal ion concentration in solution (mg/L), V is the volume of the medium (L) and m is the amount of the pumice used for adsorption (g).

After filtration, filter paper and glass were washed with 0.1 M HNO_3 several times. The amount of Cd(II) in the washing solution was determined with AAS and found to be lower than the detection limit of the AAS, which is 0.0001 mg/L. This loss of Cd(II) was therefore ignored in the measurements.

Experimental design and optimization

Parameter screening by Fractional Factorial Design (FFD)

Initial screening of the most influential adsorption parameters affecting Cd(II) adsorption onto pumice was conducted by 2^{6-2} FFD. FFD is a powerful technique for screening important variables and has successfully been applied by researchers [18,19]. Through screening experiments, the important factors can be identified and then be investigated more thoroughly in subsequent experiments. In general, factorial designs are most efficient for this type of screening experiment [20]. Nevertheless, as the number of factors in a 2^k factorial design increases, the number of runs required for a complete replicate of the design rapidly outgrows the resources of most experimenters. For example, a complete replicate of the 2^6 design requires 64 experiments. If the experimenter can reasonably assume that certain high-order interactions are negligible, information on the main effects and low-order interactions may be obtained by running only a fraction of the complete factorial experiment [20,21].

In our study, in order to determine the most influential parameters effecting Cd(II) adsorption, six parameters (pH, temperature, initial Cd(II) concentration, contact time, agitation speed, particle size) were chosen according to literature [22,23]. Each variable was represented at two levels, high and low, denoted by (+) and (-) signs, respectively. The low and high values of parameters are shown in Table 2. Design Expert 8.0.1 (trial version) was used for regression analysis of the obtained experimental data. The quality of the fit of the first-order model equation was expressed

Table 2. Range of parameters studied in the FFD for Cd(II) adsorption.

Code	Parameter	Low level (-1)	High level (+1)
X_1	pH	2	7.5
X_2	Initial Cons. (C_o, mg/L)	5	100
X_3	Contact time (min.)	10	150
X_4	Temperature (°C)	15	40
X_5	Agitation speed (rpm)	130	650
X_6	Particle size (mm)	120	180

by the coefficient, R^2, and its statistical significance was determined by an F-test in the same program. The significance of the effect of each variable on Cd(II) adsorption was measured using a t-test [17].

Determination of ranges near optimum

Based on the fitted first-order model obtained from the 2^{6-2} Fractional Factorial Design, steepest ascent experiments were constituted. The direction of steepest ascent (descent) is the direction in which response increases (decreases) most rapidly. This direction is parallel to the normal to the fitted response surface. One usually takes as the path of steepest ascent (descent) the line through the center of the region of interest and normal to the fitted surface. Thus, the steps along the path are proportional to the regression coefficients, β_i, obtained from FFD [17].

Optimization of adsorption conditions with Central Composite Design (CCD)

The CCD was applied using Design-Expert 8.0.1 (trial version). The total number of experiments with three variables found to be the most influential parameters according to FFD results was *20 (= 2k + 2*^{k} *+ 6)*, where *k* is the number of independent variables. Fourteen experiments were augmented with six replications at the center values (zero level) to evaluate the pure error. In the regression equation, the test variables were coded according to the Eq. 2:

$$X_i = \frac{X_i - X_0}{\Delta X} \qquad (2)$$

Where x_i is the dimensionless coded value of the ith independent variable, X_0 is the value of X_i at the center point and ΔX is the step change value. The following empirical second-order polynomial model Eq. 3 explains the behavior of system:

$$\hat{y}_n = \beta_o + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \qquad (3)$$

Where, $\hat{y}_n$ is the response, β_0 is the constant coefficient, x_i (i = 1–3) are non-coded variables, β_is are the linear, and β_{ii}s are the quadratic, and β_{ij}s (i and j = 1–3) are the second-order interaction coefficients. In addition, the residuals, ε_n, for each experiment were computed as difference between y_n and $\hat{y}_n$, which are the residual of *n*th experiment, observed response and predicted response, respectively.

Data was processed for Eq. (3) using Design-Expert 8.0.1 program including ANOVA to obtain the interaction between the process variables and the response. The quality of the fit of polynomial model was expressed by the coefficient of determination, R^2, and it is statically significance was checked by the F-test in the same program.

Determination of maximum points

The second-order model determined from Eq.3.is adequate for the optimal points. A general mathematical solution can be obtained from Eq. 4 for the location of the stationary point [17, 23]. Writing the second order model in matrix notation, we have;

$$y = \beta o + x'b + x'Bx_s \qquad (4)$$

Where,

$$X_S = \begin{bmatrix} X_1 \\ X_2 \\ X_k \end{bmatrix}, \quad b = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \beta_k \end{bmatrix} \quad \text{and}$$

$$B = \begin{bmatrix} \beta_{11} & \beta_{12}/2 & \beta_{1k}/2 \\ \text{Sym.} & \beta_{22} & \beta_{2k}/2 \\ \text{Sym} & \text{Sym.} & \beta_{kk} \end{bmatrix}$$

That is, b is a (kx_1) vector of the first order regression coefficient and B is a (kxk) symmetric matrix whose main diagonal elements are the pure quadratic coefficients (β_{ii}) and whose off-diagonal elements are one half of the mixed quadratic coefficients (β_{ij}, $i \neq j$). The stationary points (X_s) are the solution of Eq. 5.

$$x_S = -\frac{1}{2} B^{-1} b \qquad (5)$$

RESULTS AND DISCUSSION

Determination of the most effective parameters

The screening experiments were designed through Design-Expert trial version to evaluate the impact of six factors, medium pH, initial Cd(II) ion concentration, contact time, temperature, agitation speed and particle size. The levels of uncoded values of the tested parameters and the observed responses were shown in Table 3. The adsorbed Cd(II) ions amount (mg) per unit absorbent (g), in each run, was taken as response. Based on the statically analysis (data not shown), pH, Cd(II) ion concentration and temperature were evaluated as the most significant variables effecting Cd(II) adsorption. First order model, Eq. 6 obtained from FFD experiments, represents the effect of the tested parameters on the response.

As it is clear from Eq. 6, medium pH, initial Cd(II) concentration and temperature have the most significant effect on the adsorbed amount of Cd(II). Similar observations have reported in previous studies [24-26]. Moreover, based on the statically analysis (data not shown), three parameters, medium pH, initial Cd(II) concentration and temperature, have a significant effect at the probability level of 90% for Cd(II) adsorption on pumice.

The method of steepest ascent

Although FFD is an important tool for screening the tested variables affecting the Cd(II) adsorption, it was unable to predict the optimum region of the variables. In these cases, the steepest ascent method is essential for determination the levels the most neighboring to optimum point.

Based on the coefficients in first-order model equation obtained from Eq. 6, the path of steepest ascent (descent) was applied to find proper direction increasing or decreasing the significant variables determined with FFD according to their signs in the Eq. 6 while all the other variables were fixed at the center level of the FFD. Experimental design and corresponding responses were represented in Table 4. The response reached a optimum in experiment 5 in which medium pH interval was 6.51 and 7.39, initial Cd(II) concentration interval was 96.10 and 117.90 mg/L and medium temperature interval was 32.50 and 35°C, respectively.

$$\textbf{\textit{Adsorbed Cd(II) amount (mg/g)}} = -1.93378 + 0.16361\,[\mathbf{pH}] + 0.014114\,[\mathbf{C_o}] + 2.00315\text{E-}03\,[\textbf{Contact Time}] + 0.022828\,[\textbf{Temperature}] + 3.22002\text{E-}04\,[\textbf{Agitation speed}] + 3.38485\text{E-}03\,[\textbf{Particle size}] \qquad (6)$$

Table 3. FFD for determination of the important variables affecting the Cd(II) ion adsorption.

Run	pH	C_o (mg/L)	Contact Time (min)	Temperature (°C)	Agitation Speed (rpm)	Particle Size (mm)	Adsorbed Amount (mg/g Cd(II))
1	4.75	52.50	80.00	27.50	390.00	150.00	1.38
2	2.00	100.00	10.00	40.00	650.00	120.00	1.54
3	2.00	100.00	150.00	15.00	130.00	120.00	0.25
4	7.50	5.00	150.00	40.00	130.00	120.00	1.24
5	2.00	100.00	10.00	15.00	650.00	180.00	0.59
6	2.00	5.00	150.00	15.00	650.00	180.00	0.01
7	4.75	52.50	80.00	27.50	390.00	150.00	1.31
8	7.50	100.00	150.00	15.00	650.00	120.00	1.70
9	2.00	5.00	150.00	40.00	650.00	120.00	0.0144
10	4.75	52.50	80.00	27.50	390.00	150.00	1.35
11	7.50	5.00	150.00	15.00	130.00	180.00	0.234
12	2.00	5.00	10.00	15.00	130.00	120.00	0.00787
13	7.50	100.00	10.00	15.00	130.00	180.00	2.05
14	2.00	5.00	10.00	40.00	130.00	180.00	0.015
15	7.50	100.00	10.00	40.00	130.00	120.00	1.56
16	7.50	5.00	10.00	15.00	650.00	120.00	0.242
17	7.50	100.00	150.00	40.00	650.00	180.00	3.70
18	7.50	5.00	10.00	40.00	650.00	180.00	0.24
19	4.75	52.50	80.00	27.50	390.00	150.00	1.34
20	2.00	100.00	150.00	40.00	130.00	180.00	1.34

Optimization

The neighborhood of the optimum point was determined by steepest ascent combined with FFD. Thereafter, optimization of the removal of Cd(II) ions from aqueous solutions for three parameters were carried out with CCD. Together with six replications conducted at the center values (zero level) to evaluate the pure error, totally twenty experiments were made for optimization. Order of the experiments and levels of the each parameter in coded, -α, -1, 0, +1, + α, and uncoded form and the observed responses were shown in Table 5. The model equation for uncoded (real) values of quadratic model fitting of experimental results was presented in Eq. 7.

The statistical significance of the quadratic model was evaluated by the analysis of variance (ANOVA) (data not shown). The low p value shows that the second-order quadratic model for observed results is significant [17]. The value of the determination of coefficient (R^2=0.90) indicates that 90 % of the variability in the response is explained by the model.

Table 4. Experimental design of steepest ascent and corresponding responses for Cd(II) adsorption.

Exp. No	pH	C_o (mg/L)	Temperature (°C)	Adsorbed amount (mg/g Cd(II))
Central point	4.75	52.50	27.50	1.44
1	5.19	63.40	28.75	1.61
2	5.63	74.30	30.00	1.60
3	6.07	85.20	31.25	1.62
4	6.51	96.10	32.50	1.77
5	6.95	107.00	33.75	1.80
6	7.39	117.90	35.00	1.75

Plot of observed removal of Cd(II) ions versus those obtained from Eq. 7 was shown in Figure 1. The figure proves that the predicted data of the response from the empirical model is well in agreement with the observed ones.

Figure 2 shows the simultaneous effects of initial pH and initial Cd(II) concentration on Cd(II) adsorption capacity by pumice at a fixed temperature of 34°C. As can be seen in Figure

$$\textbf{\textit{Adsorbed Cd(II) amount (mg/g)}} = -14.40359 + 0.14621\,\mathbf{[C_o]} + 1.72937\,\mathbf{[pH]} + 0.077403\,\mathbf{[Temperature]} - 0.12689\,\mathbf{[pH^2]} - 6.17757\text{E-}04\,\mathbf{[C_o^2]} - 1.54079\text{E-}03\,\mathbf{[Temperature^2]} - 1.25\text{E-}03\,\mathbf{[pH.C_o]} + 5.625\text{E-}03\,\mathbf{[pH.Temperature]} - 1.5625\text{E-}04\,\mathbf{[C_o.Temperature]} \quad (7)$$

Table 5. CCD results for Cd(II) adsorption onto pumice.

Run	pH	C_o (mg/L)	Temperature (°C)	Adsorbed Amount (mg/g Cd(II))
1	7.00	105.00	40.73	0.66
2	6.50	115.00	38.00	0.62
3	6.16	105.00	34.00	0.62
4	7.50	95.00	38.00	0.59
5	7.00	121.82	34.00	0.60
6	7.50	115.00	30.00	0.66
7	7.00	105.00	34.00	0.75
8	7.00	105.00	34.00	0.68
9	6.50	95.00	30.00	0.62
10	7.00	105.00	27.27	0.69
11	7.50	95.00	30.00	0.59
12	7.00	105.00	34.00	0.75
13	7.84	105.00	34.00	0.69
14	6.50	115.00	30.00	0.69
15	6.50	95.00	38.00	0.55
16	7.00	105.00	34.00	0.72
17	7.00	105.00	34.00	0.78
18	7.50	115.00	38.00	0.61
19	7.00	88.18	34.00	0.54
20	7.00	105.00	34.00	0.75

2, although rising from 6.50 to 7.00 of pH of the Cd(II) solution sharply increased adsorption capacity, then adsorption capacity decreased with increased pH. As the pH increases, the negative charge density on adsorbent surface increases due to deprotonation of the metal binding sites. Similar comment was made in a previous study [27]. Maximum adsorption was approximately observed at pH 7. They concluded that the increase in metal removal with increase in pH can be explained on the basis of a decrease in competition between proton and the metal cations for the same functional groups and by the decrease in positive charge of the adsorbent which results in a lower electrostatic repulsion between the metal cations and the surface.

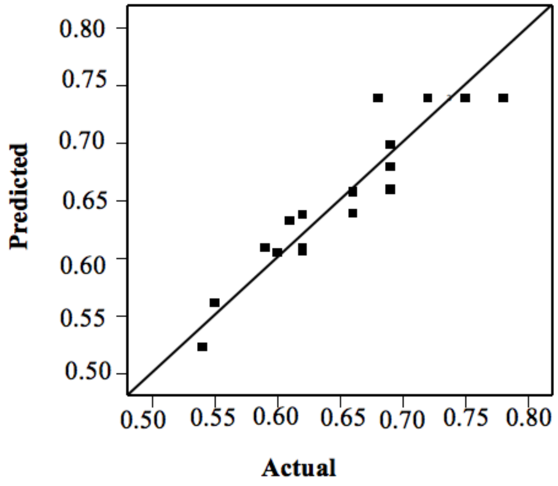

Figure 1. Observed Cd(II) ion removal versus predicted values obtained from quadratic model.

An adsorption mechanism for high pH can be explained by Eq. 8 and 9 [23]. At low pH values, the low adsorption is due to the increase in positive charge density on the surface sites, and thus, electrostatic repulsion occurred between the metal ions (M^{2+}: Cd^{2+}) and the edge groups with positive charge ($Si\text{-}OH_2^+$) on the surface following Eq. 10.

$$-SiOH + OH^- \leftrightarrow -SiO^- + H_2O \quad (8)$$

$$-SiO^- + M^{2+} \leftrightarrow -Si\text{-}O\text{-}M^{2+} \quad (9)$$

$$-SiOH + H^+ \rightarrow -Si\text{-}OH_2^+ \quad (10)$$

pH is an important factor influencing the adsorption of heavy metals. The pH dependence of metal uptake is related to both the functional groups on the adsorbent surface and the metal chemistry in solution, which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [28,29]. At lower pH, charge density on the binding sites became positive due to protonated active sites. Because of this, metal cations and protons compete for binding sites on adsorbent surface. Consequently, heavy metal adsorption decreases [30].

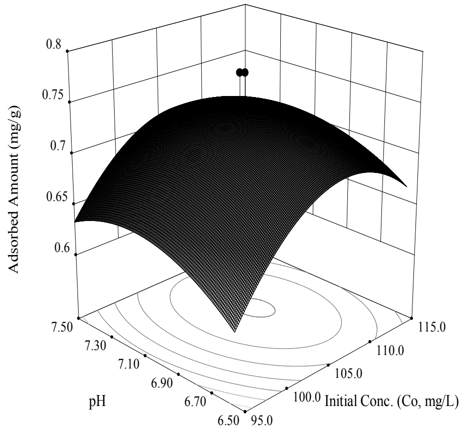

Figure 2. Simultaneous effect of medium pH and initial Cd(II) concentration on Cd(II) adsorption (a fixed temperature of 34°C).

Cd(II) adsorption capacity onto pumice sharply increased with initial Cd(II) concentration increasing from 95 to 105 mg/L and then did not change with further increasing in initial Cd(II) concentration. This result can be explained in the way of the interaction of Cd(II) ions and adsorbent. At the lower Cd(II) concentration, the ratio of Cd(II) ions to the available adsorption sites also increases [31,32]. As a result, adsorbed Cd(II) amount also increases but with increasing Cd(II) concentration, saturation of active sites on adsorbent surface decreases adsorbed Cd(II) amount.

Figure 3 shows the combined effects of temperature and initial Cd(II) concentration on Cd(II) adsorption capacity by pumice at a fixed pH of 7.00. As seen in Figure 3, temperature indicated a negative effect on removal of Cd(II) ions onto pumice. Cd(II) ions removal capacity for pumice slowly increased with increasing temperature from 30 to 33°C and approximately reached to maximum value around 33°C. Then adsorption capacity of Cd(II) ions onto pumice sharply decrease with increasing temperature and this result shows adsorption is exothermic in nature. Some researches [33,34] reported that Cd(II) adsorption on different adsorbents was exothermic in nature and our works verified this idea as well. The decrease in adsorption with the increase of temperature may be due to a tendency for the Cd(II) ions to escape from the solid phase to the bulk phase with an increase in the temperature of the solutions [34]. Additionally, the decrease in the removal at increasing temperatures can also be attributed to the increased solubility of metal at relatively higher temperatures [35]. Simultaneous effects of temperature and pH on removal capacity of Cd(II) for pumice at a fixed initial concentration of 105 mg/L are represented in Figure 4.

Determination of the optimum values for adsorption conditions

The optimum points of the most important parameters to maximize the adsorption of Cd(II) were evaluated by application of Eq. 5. Xs, b, and B matrixes in Eq. 5 were arranged by Eq. 7, which includes uncoded values of the parameters. Xs, b, and B matrixes were formed as follows [17,23].

$$X_s = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix}, \quad b = \begin{bmatrix} 0.14621 \\ 1.72937 \\ 0.077403 \end{bmatrix} \quad \text{and}$$

$$B = \begin{bmatrix} -6.17757E-04 & -6.25E-04 & 7.8125E-05 \\ -6.25E-04 & -0.12689 & 2.8125E-03 \\ 7.8125E-05 & 2.8125E-03 & -1.54079E-03 \end{bmatrix}$$

From the solution of the above matrixes with Eq. 5, the optimum values for Cd(II) adsorption were 7.01 medium pH, 107.14 mg/L initial Cd(II) ion concentration and 32.48°C temperature. Under the evaluated optimum experimental conditions, maximum Cd(II) adsorption calculated from quadratic model was 0.827 mg Cd(II)/ g adsorbent and corresponding removal efficiency of Cd(II) was 76.51%. Moreover, this result was verified with experimental data.

A comparison between different some adsorbents in literature and pumice is given in Table 6. As can be seen in Table 6, the Cd removal capacities of other some adsorbents such as river bed sand, perlite and wheat bran were lower than used pumice. However, other adsorbent's capacities were higher than pumice. This may be attributed to the effects of particle size distribution, surface area, morphology, surface structure and related properties [36]. The values of the adsorption capacities for pumice may not be highest but it has a number of advantages over most of the adsorbents used for the purpose. It is available in plenty in all parts of world and it has low cost, it is non-toxic and practically does not require any treatment prior to application. The cost of adsorbents is an important parameter for adsorption process. Pumice has a low cost than the other traditional adsorbents. Thus, the comparison suggests that pumice has a potential for use as Cd ions from aqueous solutions.

ted value

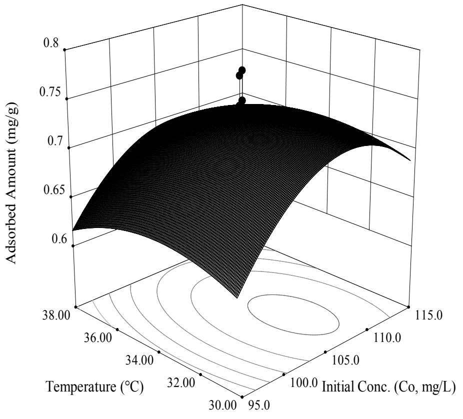

Fig. 3. Simultaneous effects of temperature and initial Cd(II) concentration on Cd(II) adsorption (a fixed pH of 7).

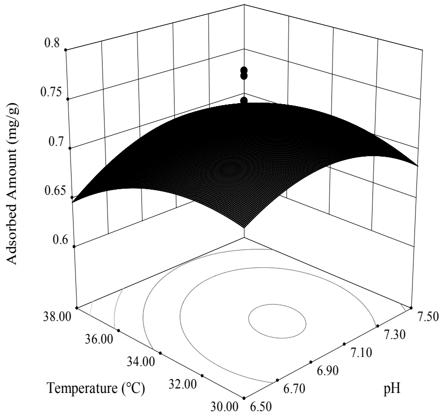

Fig. 4. Simultaneous effects of temperature and pH on Cd(II) adsorption (a fixed initial concentration of 105 mg/L).

Table 6. Comparison between pumice and other adsorbents discussed in the literature.

Adsorbent	Cd(II) Adsorption (mg/g)	Ref.
River bed sand	0.15	[37]
Granular activated carbon	3.40	[38]
Almond-shell carbon	2.70	[39]
M. rouxii	3.80	[40]
Perlite	0.64	[41]
Wheat bran	0.70	[42]
Coconut copra meal	4.92	[43]
Kaolinite	9.90	[44]
Pumice	**0.827**	**This work**

CONCLUSION

A multi-step RSM was used in optimizing adsorption conditions for Cd(II) adsorption onto pumice. Firstly, (FFD) was efficiently used to screen factors affecting Cd(II) adsorption significantly. Secondly, the method of steepest ascent was used to determine the neighborhood of optimum point of the most influential parameters for Cd(II) adsorption. Finally, CCD was used to determine the optimum values of the effective factors, which are pH, initial Cd(II) concentration and temperature. A quadratic model obtained from CCD matched the experimental dat. Based on quadratic model, the optimized values of these factors are determined as 7.01, 107.14 mg/L, 32.48°C for pH, Cd(II) concentration and temperature, respectively. Under these optimum conditions, maximum adsorbed Cd(II) amount calculated from quadratic model was 0.827 mg Cd(II)/ g adsorbent and corresponding removal efficiency was % 76.51. It is concluded that pumice can be effectively used for heavy metal adsorption and has an important potential for Cd(II) adsorption.

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