Cd (II) Removal from Aqueous Solutions by Adsorption on Henna and Henna with Chitosan Microparticles Using Response Surface Methodology

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ABSTRACT: *In this research, the capabilities of Henna and Henna with chitosan microparticles adsorbents were studied in order to remove the ion Cd (II). Response Surface Method (RSM) and Central Composite Design (CCD) were used to minimize the number of experiments (21 runs) for Henna and (26 runs) for the Henna with chitosan microparticles. The parameters were pH (2-9), initial solution concentration [10-100 mg/L (ppm)], adsorbent dosage (0.1-1 g) and process time (20-150 min). It was concluded that Cd (II) removal increased from 13.78% to 70.06% with increasing the pH from 2 to 9 (maximum adsorption was at pH 9) for Henna and 82.81% to 97.60% for the Henna with chitosan microparticles. The Cd (II) removal was decreased from 78.73% to 40.44% for Henna and 96.47% to 90.37% for the Henna with chitosan microparticles with increasing the initial solution concentration (from 10 to 100 ppm). Furthermore, the Cd (II) removal was increased from 37.5% to 64.59% for Henna and from 86.74% to 97.76 % for the Henna with chitosan microparticles with the adsorbent dosage increment (from 0.1 to 1 g). The error for the optimum point between the statistical data and experimental ones were at 1.53% for Henna and at 1.61% for the Henna with chitosan microparticles. The Langmuir and Freundlich isotherm models were applied as the adsorption mechanism. Two correlations (with R^2=0.9750 for Henna and R^2=0.8538 for the Henna with chitosan microparticles) between the Langmuir model and experimental data were investigated although Freundlich model showed the better agreements between the theoretical data and experimental ones (R^2=0.9949 for Henna and R^2=0.9955 for the Henna with chitosan microparticles). It also showed that the Henna with chitosan microparticles is a fantastic adsorbent for Cd (II) removal.*

KEYWORDS: *Adsorption; Biomass; Chitosan; Heavy metals; Wastewater.*

INTRODUCTION

Heavy metal contamination in various water recourses is a great concern due to the toxicity effect on human, animals, and plants. One of these metals is cadmium [Cd (II)] which is released to the environment via combustion of fossil fuels, metal production industries (such as zinc, iron and steel production), cement production,

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1021-9986/2019/3/267-281 *152/$/6.05*

electroplating, batteries manufacturing and pigments preparation. Cadmium (II) in water (even in ppb or ppm) can cause muscular cramps, chronic pulmonary problems, renal degradation, proteinuria, skeletal deformity and testicular atrophy [1].

The maximum concentration for Cd (II) in drinking water is at 0.003 ppm according to the World Health Organization (WHO) report [2].

There are several technologies such as electro coagulation, ion exchange and emulsion liquid membrane for heavy metals removal [3-5]. Adsorption process also is one of the most popular separation methods due to the simplicity of operation, cheapness, high efficiency, easy recovery, regeneration capacity and sludge-free operation [6]. *Jung et al.* used nano-sized carbon in alginate beads (NCB) for Co (II) and Ni (II) removal from the aqueous solutions [7]. In another research, Procaine hydrochloride immobilized polyurethane foam (PUFs) as a rapid and selective chemical was used to remove cadmium (II) from water [8]. *Nabel et al.* purified industrial wastewater contaminated with copper and cobalt by the modified chitosan [9]. *Behbahani et al.* successfully applied the functionalized MCM-41 nanoporous silica with 3, 4-dihydroxybenzaldehyde for the copper, silver, gold and palladium reduction in the real samples [10]. Due to the economical limitations, several natural adsorbents such as sawdust, biomasses (corn leaves, rice husk, wheat bran, banana, pea peels and etc) were widely applied [11-15]. An ideal adsorbent for heavy metal ions removal should have a large surface area, high adsorption capacity, suitable pore size, mechanical stability, compatibility, easy accessibility, regeneration ability, economical feasibility and high selectively [16].

Henna (grayish green leaves) is an abundant cheap plant in the south of Iran (Kerman, Hormozgan and Balochistan) and tropical regions in Asia and Africa [17] which can be used as an adsorbent due to having the above benefits. Furthermore, a natural biopolymer such as chitosan which has alkaline N-deacetylation of chitin can properly adsorb the heavy metal ions due to having reactive hydroxyl and amino groups [18]. It has fantastic properties such as biodegradability, bioactivity, biocompatibility, non-toxicity, cheapness, and abundance although it has some lacks such as low acid stability, inadequate mechanical properties, low thermal stability, resistance against mass transfer, low porosity and surface areas [19]. Therefore, chitosan microparticles can be used to improve the lack of chitosan [18].

There are Cd (II) ions in the wastewater of a lot of industries. This heavy metal (in ppm or ppb) is very harmful and can make several diseases such as muscular cramps, chronic pulmonary problems, renal degradation, proteinuria, skeletal deformity, and testicular atrophy. Since Henna is a cheap and abundant biomass (in some countries) with several active sites for heavy metals adsorption, it can widely be used in the industrial scale. Furthermore, chitosan (as a fantastic adsorbent but expensive one) can dramatically increase Henna active sites for the adsorption of heavy metals. In this research, Henna was initially used and physically mixed with chitosan microparticles. Statistical software (DoE version 7) was applied to minimize the number of experiments and optimize the process [20]. Some process parameters such as solution pH, its initial concentration in terms of cadmium (II), contact time and adsorbent dosage were chosen. CCD under RSM was applied in this work. Moreover, the interaction of parameters was carefully analyzed by the quadratic regression model and their effects on the cadmium (II) removal were correlated [18, 21].

EXPERIMENTAL SECTION

Adsorbent preparation and its test

Henna leaves were dried and then grinded and passed through the standard screens (70-100 μm). Chitosan (in microparticles) was purchased from Nano-Yakhteh supplier (Alborz Science and Research Park, Karaj, Iran) (with yellow color, the viscosity of 120 cps, D.A.C of 96.1%, soluble substances of 0.31%, ash of 0.68%, the moisture of 8.2% and 100000 meshes/500 μm). Cd (II) solutions with the required concentrations (10-100 ppm), were prepared by dissolving $Cd(NO_3)_2$ (Merck grade) in the double-distillated water. All the batch tests were done in a beaker with volume of 250 cm^3. pH was set by 0.1 M HCl and NaOH. All of the experiments were conducted at room temperature.

The adsorbents (Henna and Henna with chitosan microparticles) with various concentrations were used for different solutions at various times and pH. After each process, the solid phase was separated by the Whatman filter paper (no.42). In order to prevent Cd (II) sedimentation in the solution and provide acidified qualification, few drops of hydrochloric acid with high

density was added to each filtrated sample. Then, each sample was tested by atomic absorption (model: AA-680). Furthermore, Infrared Spectrometer Transfer (FT-IR) (model: Unicam 5000) was used to find the adsorbent functional groups. The Scanning Electron Microscope (SEM) (model: Pro X) was used to see the adsorbent morphology before and after adsorption process.

Cd (II) removal amount from solution and isotherms

The Cd (II) removal percentage was calculated using the following equation [22]:

$$R\% = \frac{(c_i - c_e)}{c_i} \times 100 \quad (1)$$

$$q_{eq} = \frac{c_i - c_e}{m} \times V \quad (2)$$

Where, c_i (mg/L) is the first concentration and c_e (mg/L) is the equilibrium concentration, respectively. V (L) is the volume of solution and m (g) is the mass of adsorbent. Equation (2) is an equilibrium relation which considers the adsorption isotherm. The isotherms of Langmuir and Freundlich were used to stating the Cd (II) removal for both adsorbents. Freundlich model demonstrates the heterogeneity of the adsorbent surfaces while the Langmuir model implies the restricted part availability of the adsorbent surface.

The linear model of Langmuir isotherm hypothesizes that the monolayer absorption reversibly happens on the contiguous area of an adsorbent [23, 24]:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{c_e}{q_{max}} \quad (3)$$

Where q_{max} (mg/g) is the surface concentration in the monolayer cover. K_L is a coefficient related to the adsorption energy.

The amount of q_{max} and K_L are obtained by the linear regression of $\frac{c_e}{q_e}$ versus C_e. The Freundlich model (linear form) can be shown as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where, K_f and n are the constants of the Freundlich equation, respectively. In fact, K_f is a coefficient in terms of the adsorbent capacity and 1/n shows the reaction degree.

Experiments design and statistical analysis

Response Surface Methodology (RSM) includes a set of useful statistical and mathematical methods for experiment design and mutual effects of parameters consideration on the process. The relation between a response and independent variables is shown by a polynomial. The graphical outputs are called levels of response and can be used for the description of the unique or mutual effects of variables on the response [25].

The goal of RSM is to optimize the surface of the response that is affected by various parameters of the process [26]. According to Table 1, four parameters in five surfaces for Henna [pH, time (min), Henna dosage (g) and initial concentration of Cd (II) solution (ppm)] and five parameters for the Henna with chitosan microparticles [pH, time (min), Henna dosage (g), chitosan dosage (g) and initial concentration of Cd (II) solution (ppm)] were chosen. Then, the regression analysis was done to determine the coefficients of the response model and standard error by the Design of Expert [27].

The process response and four independent variables can be modeled by a quadratic equation [20]:

$$Y = \beta_0 + \sum_{i=0}^{4} \beta_i x_i + \sum_{i=0}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{4} \sum_{j=1}^{4} \beta_{ij} x_i x_j \quad (5)$$

Where Y is the response variable, β_0 is the intercept, β_i is the regression coefficient calculated from the obtained values and x_i is the coded surfaces from the dependent variables. $x_i x_j$ and x_i^2 are the interaction and quadratic ones [27,28].

The quality of the fitness of the model equation is assessed by R^2 and adjusted R^2. The adjusted R^2 modifies the value of R^2 for the sample amount and the number of expressions in the model [29].

In order to optimize four variables (for Henna) and five variables (for the Henna with chitosan microparticles), twenty one experiments were designed (for Henna) and twenty six experiments were designed (for the Henna with chitosan microparticles) by software. The matrix related to the design and the residual concentrations of Cd (II) as the response was shown in Table 2.

Table 1: The applied parameters range for Henna and blends of Henna with chitosan microparticles.

Variables	Surfaces for Henna					Surfaces for blends of Henna with chitosan microparticles				
	+α	+1	0	-1	-α	+α	+1	0	-1	-α
pH	9	7.58	5.5	3.42	2	9	7.42	5.5	3.58	2
Henna dosage (g)	1	0.82	0.55	0.28	0.1	1	0.8	0.55	0.3	0.1
Chitosan dosage (g)	-	-	-	-	-	1	0.8	0.55	0.3	0.1
Contact time (min)	150	124	85	46	20	150	120	85	49	20
Initial concentration (ppm)	100	82	55	28	10	100	80	55	30	10

Table 2: The central composite design with four variables and the residual concentration (and removal percentage) of Cd (II) for Henna and blends of Henna with chitosan microparticles.

Trial no.	pH	Time (min)	Henna dosage (g)	Chitosan dosage (g)	Initial Concentration (ppm)	Residual Concentration (ppm)	Removal (%)
1.00	5.5	85	0.55	-	55	25.97	52.78
2.00	5.5	150	0.55	-	55	28.24	48.64
3.00	5.5	85	0.55	-	10	2.13	78.73
4.00	7.58	46	0.82	-	28	7.47	73.56
5.00	3.42	46	0.82	-	82	47.16	42.32
6.00	5.5	85	0.55	-	55	25.02	54.50
7.00	5.5	85	0.55	-	100	59.55	40.44
8.00	7.58	46	0.28	-	82	48.42	40.77
9.00	5.5	85	0.55	-	55	19.95	63.72
10.00	3.42	124	0.82	-	82	38.91	52.40
11.00	9.00	85	0.55	-	55	16.46	70.06
12.00	5.5	85	1.00	-	55	19.47	64.59
13.00	3.42	46	0.28	-	28	9.54	66.20
14.00	7.58	124	0.82	-	28	10.86	61.52
15.00	2.00	85	0.55	-	55	47.42	13.78
16.00	7.58	124	0.28	-	82	44.19	45.94
17.00	3.42	124	0.28	-	28	9.49	66.39
18.00	5.5	20	0.55	-	55	24.44	55.56
19.00	5.5	85	0.55	-	55	24.97	54.60
20.00	5.5	85	0.1	-	55	34.37	37.50
21.00	5.5	85	0.55	-	55	24.91	54.69

Table 2: Continued

Trial no.	pH	Time (min)	Henna dosage (g)	Chitosan dosage (g)	Initial Concentration (ppm)	Residual Concentration (ppm)	Removal (%)
1.00	5.5	85	0.55	1.00	55	1.22	97.76
2.00	5.5	85	1.00	0.55	55	1.34	97.55
3.00	5.5	20	0.55	0.55	55	2.55	95.36
4.00	7.42	49	0.30	0.80	79.71	11.53	85.53
5.00	5.5	85	0.55	0.55	100	9.62	90.37
6.00	5.5	85	0.55	0.55	55	4.85	91.17
7.00	5.5	85	0.55	0.10	55	7.29	86.74
8.00	7.42	49	0.80	0.30	79.71	6.71	91.56
9.00	5.5	85	0.55	0.55	55	4.79	91.28
10.00	5.5	85	0.55	0.55	55	4.81	91.24
11.00	3.58	120	0.30	0.80	79.71	7.99	89.97
12.00	5.5	85	0.10	0.55	55	14.66	73.33
13.00	5.5	150	0.55	0.55	55	2	96.36
14.00	7.42	49	0.80	0.80	30.29	2.36	92.18
15.00	7.42	120	0.30	0.30	79.71	18.33	76.99
16.00	9.00	85	0.55	0.55	55	1.31	97.60
17.00	5.5	85	0.55	0.55	10	0.35	96.47
18.00	3.58	120	0.80	0.80	30.29	0.61	97.97
19.00	7.42	120	0.80	0.30	30.29	0.76	97.47
20.00	5.5	85	0.55	0.55	55	4.84	91.19
21.00	3.58	49	0.30	0.30	30.29	2.03	93.29
22.00	3.58	120	0.80	0.30	79.71	3.85	95.16
23.00	7.42	120	0.30	0.80	30.29	1.51	94.99
24.00	2.00	85	0.55	0.55	55	9.45	82.81
25.00	5.5	85	0.55	0.55	55	4.86	91.16
26.00	3.58	49	0.80	0.80	79.71	1.82	97.71

The system behavior was inspected by a quadratic equation as below:

for Henna adsorbent:

$$Y = +24.99 - 4.43X_1 - 9.2X_2 - 0.2X_3 + 17.07X_4 - 0.59X_1X_2 - 0.07X_1X_3 - 9.84X_1X_4 + 0.93X_2X_3 - 3.56X_2X_4 - 1.98X_3X_4 + 0.064X_1^2 + 1.85X_2^2 - 0.13X_3^2 + 1.46X_4^2 \quad (6)$$

for the Henna with chitosan microparticles:

$$Y = 4.32 - 3.66X_1 - 1.66X_2 - 0.15X_3 + 2.23X_4 + 2.55X_5 - 0.48X_1X_2 - 1.88X_1X_3 - 1.33X_1X_4 + 2.78X_1X_5 - 2.66X_2X_3 - 0.71X_2X_4 - 2.57X_2X_5 + 0.49X_3X_4 - 1.91X_3X_5 + 1.78X_4X_5 + 1.06X_1^2 - 0.071X_2^2 - 0.67X_3^2 + 0.27X_4^2 + 0.15X_5^2 \quad (7)$$

Table 3: Analysis of variance (ANOVA) for quadratic model for Cd (II) adsorption on Henna and blends of Henna with chitosan microparticles.

Source of variation	Sum of Squares	DF	Mean Square	F-Value	P>F
Model	4086.97	14	291.93	8.11	0.0085
Residual	216.09	6	36.01		
Lack of fit	140.21	2	70.11	3.70	0.1233
Pure error	75.88	4	18.97		
Total	4303.06	20			
R^2=0.9498 CV=11.07% DF: Degree of freedom for Henna					
Model	998.25	20	49.91	213	< 0.0001
Residual	1.17	5	0.23		
Lack of fit	1.16	1	1.16	439.10	< 0.0001
Pure error	0.011	4	2.644×10^{-3}		
Total	999.42	25			
R^2=0.9988 CV=0.53% DF: Degree of freedom for blends of Henna with chitosan microparticles					

According to equation 6, Y is the residual concentration of Cd (II) in the solution. X_1, X_2, X_3, and X_4 are Henna dosage, pH, time and initial concentration of the solution in terms of Cd (II), respectively.

According to equation 7, Y is the residual concentration of Cd (II) in the solution. X_1, X_2, X_3, X_4, and X_5 are Henna dosage, chitosan dosage, time, pH and initial concentration of the solution in terms of Cd (II), respectively.

The results of the analysis of variance (ANOVA) the quadratic model is illustrated in Table 3. As shown in this table, R^2 and the adjusted R^2 are close to 1. Therefore, it shows very good agreement between the experimental data and the predicted ones. Furthermore, the associated Prob.>F value for the model is less than 0.05. It indicates that the quadratic model statistically is significant for the response and therefore it will be used for further analysis. F-value can be used for consideration of the significance of each parameter. The table indicates that the pH solution is the most significant parameter in adsorption by Henna while this is the most important parameter after Henna dosage in the adsorption through the Henna with chitosan microparticles. Furthermore, the F-value shows that the contact time does not have a significant effect on Cd (II) removal for both adsorbents [30].

RESULTS AND DISCUSSION

FT-IR analysis was used to investigate the information of possible interaction between the functional groups in adsorbents and the metal ions in solution. According to FT-IR, Henna adsorbent before adsorption (Fig. 1a) and after adsorption (Fig. 1b) has a lot of active functional groups that are able to adsorb metal ions such as Cd (II). As shown in these figures, the peaks in wavelength of 3394 cm^{-1} are related to O-H functional group while the wavelength of 2858-2926 cm^{-1} are related to the functional group of $–CH_2$. The wavelength of 1784 cm^{-1} belongs to the functional group of CO^{-3}. The wavelength of 1658 cm^{-1} is related to the functional group of –C=O and the wavelength of 1238 cm^{-1} is related to the C=N functional group. The peak of 1030 cm^{-1} is related to the functional groups of –C-O and –S=O. The functional groups of -O-P-O and $–PO_4$ emerge in the range of 515-653 cm^{-1}. The functional groups provide an electron that increases Cd (II) adsorption tendency. FT-IR analysis after adsorption of Cd (II) on the Henna shows that there are some changes in the adsorption peaks. It seems that O–H functional group (at the peak of 3394 cm^{-1}) is the most effective functional group. In fact, hydrogen of hydroxyl functional group is replaced by Cd^{2+} and H^+ is then released in the solution. This reaction will decrease pH of solution [31].

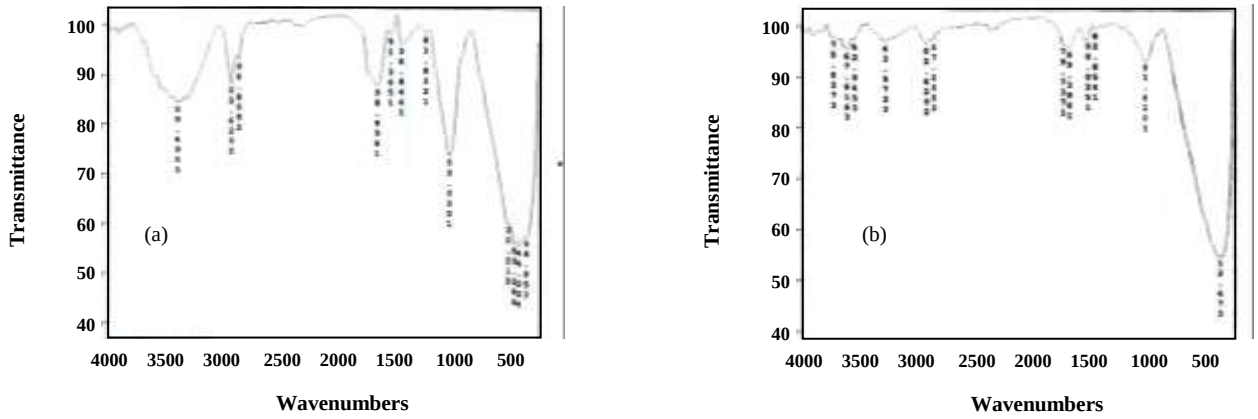

Fig. 1: FT-IR Spectra of Henna [before (a) and after (b) adsorption].

Furthermore, the functional groups generally are in the segregated status and can exchange H^+ with the metal ions (Cd^{2+}) when solution pH is more than pka (acidic segregation constant). In other words, the metal cations will not be connected to the functional groups due to separation lack of the functional groups in a solution with low pH [32]. Therefore, there is a limitation in the metal ions removal from a solution with low pH (as Cd^{2+} removal was low for the solutions with pH of 2 and less than it) [33, 34].

Figs. 2a, 2b and 2c illustrate chitosan microparticles, the Henna with chitosan microparticles FT-IR before and after the adsorption process, respectively. Fig. 2b shows that most of the peaks were strengthened in the Henna with chitosan microparticles. According to this figure, the peaks in the wavelengths of 3545, 2858-2924, 1734, 1656, 1384, 1151, 1031, 372-462 cm^{-1} are related to O-H, $–CH_2$, CO^{-3},–C=O, ─CH_3, C=N,–C-O and –S=O as well as -O-P-O and $–PO_4$ functional groups, respectively. These results show that the O-H functional group is the most effective functional group in the Cd (II) adsorption process on the Henna with chitosan microparticles. Moreover, pH affects the metal ions connection with functional groups. So, pH is an important factor in the adsorption process [35].

The SEM images of Henna before (a) and after (b) adsorption are shown in Fig. 3 (Fig. 4 also shows SEM images of pure chitosan) while the SEM images for the Henna with chitosan microparticles before (a) and after (b) adsorption are presented in Fig. 5.

According to the EDS analysis before (a) and after (b) adsorption, cadmium (II) phase is properly adsorbed on the Henna (Fig. 6) and the Henna with chitosan microparticles pores (Fig. 7).

Although Cd (II) adsorption takes place in the high pHs [36] but, Fig. 8 (for Henna) and Fig. 9 (for the Henna with chitosan microparticles) indicate that Cd (II) removal sharply increases with pH (from 2 to 7.5) while it slowly increases after 7.5. The maximum adsorption is obtained at pH of 9 for both adsorbents. A competition between proton and metal cations for adsorption on the same functional groups and reduction of positive surface charge which results in a lower electrostatic repulsion between surface and metal ions is the main reason for Cd (II) removal enhancement in high pHs. The sedimentation process is observed for solutions with pHs more than 9 (maximum pH should be adjusted at 9) although soluble hydroxyl complexes form in high pHs [37].

Adsorbent dosage is another important parameter in the metal ions adsorption. Adsorbent amount optimization is very interesting because it reduces the process costs via consumed adsorbent, contaminant and sludge production reduction [33]. Figs. 10 (for Henna) and 11 (for the Henna with chitosan microparticles) show the effect of adsorbent dosage on the level of Cd (II) removal and Cd (II) residual concentration.

As shown in these figures, the adsorbent dosage enhancement (from 0.1 to 1 g) gradually decreases the Cd (II) residual concentration for both adsorbents. However the Cd (II) residual concentration increases at the adsorbent dosage of 1 g but the adsorption efficiency does not widely increase in the more adsorbent dosages than 1 g. In fact, the adsorption efficiency increases

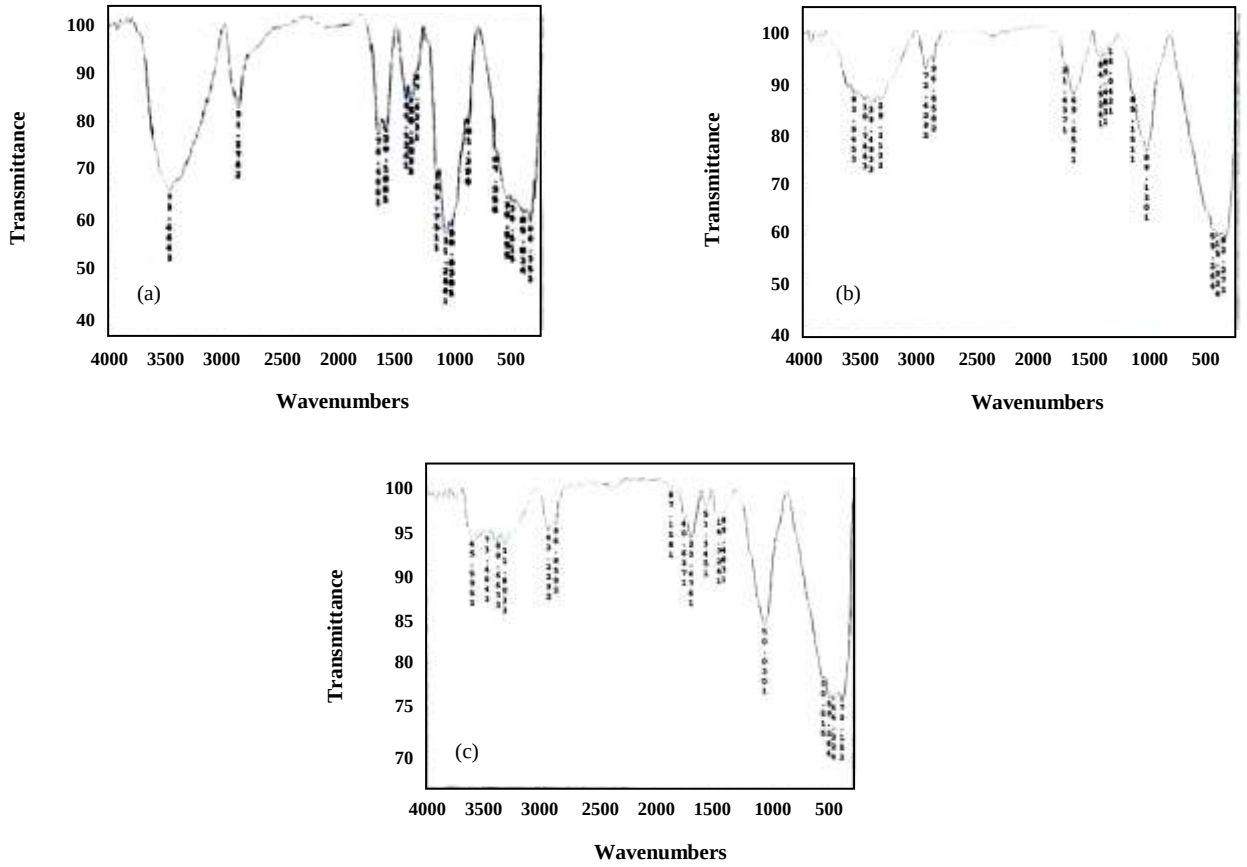

Fig. 2: FT-IR Spectra of chitosan microparticles (a) and blends of Henna with chitosan microparticles [before (b) and after (c) adsorption].

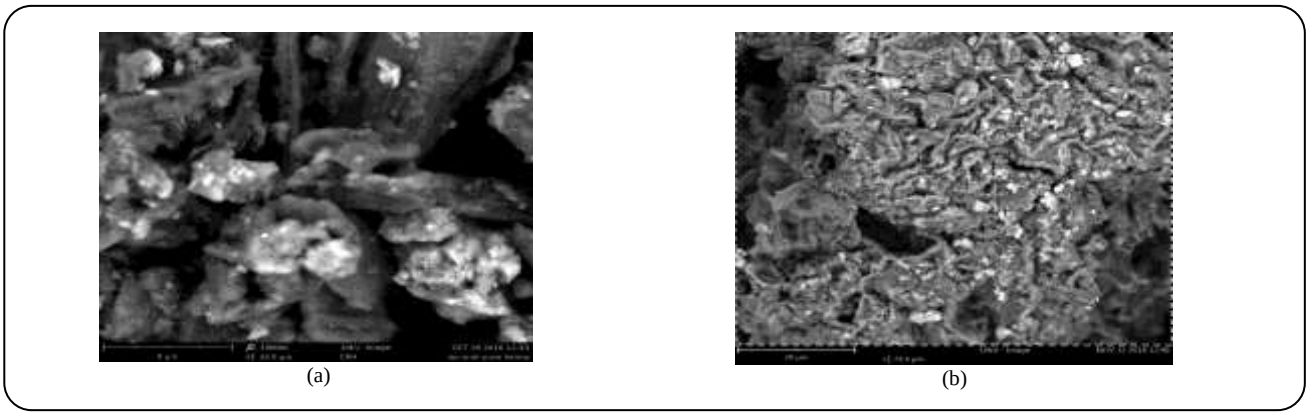

Fig. 3: SEM of Henna [before (a) and after (b) adsorption].

with adsorbent active sites when the adsorbent dosage increases [38]. The partial overlap may happen in the high dosages of adsorbent due to active site reduction [39]. The other reason is a restriction in adsorption capacity for the excessive adsorbent dosages (more than 1g). This is due to adsorbent aggregation and agglomeration which decreases total surface area and increases the energy course length [40, 41]. Figs. 12 (for Henna) and 13 (for the Henna with chitosan microparticles) show the effect of contact time and initial concentration on the Cd (II) removal.

As shown in these figures, the removal level decreases when the initial concentration increases. The reduction in adsorption level occurs with increasing the initial concentration of metal. This is due to the limitation

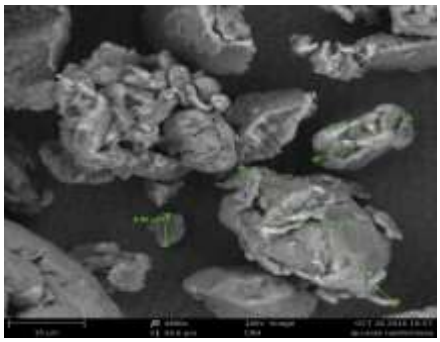

Fig. 4: SEM of chitosan.

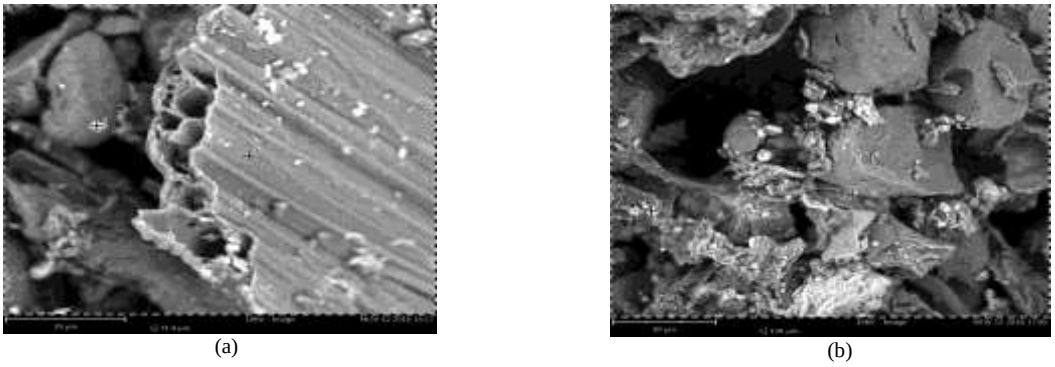

Fig. 5: SEM of blends of Henna with chitosan microparticles [before (a) and after (b) adsorption].

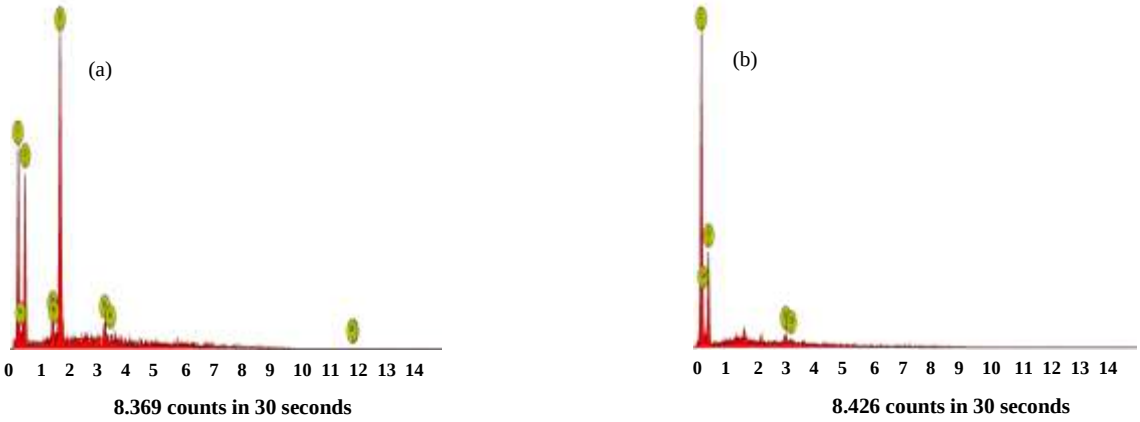

Fig. 6: EDS of Henna [before (a) and after (b) adsorption].

in the adsorbent sites [42]. The optimum time for both adsorbents is around 20 min and the adsorption decreases with increasing the time after that time. There is no change in the level of residual Cd (II) concentration with increasing the time of more than 20 min. Therefore, contact time prolong has no significant effect on adsorption. This may be due to filling the adsorbent sites. Since the number of active sites is constant for the adsorbent in each system and each active site can adsorb in a monolayer so, metal removal efficiency decreases over time [43]. According to the literature, the optimum time is around 85 min for the Cu (II) and Ni (II) adsorption on pure Henna [44]. Furthermore, the optimum contact time for reaching the equilibrium

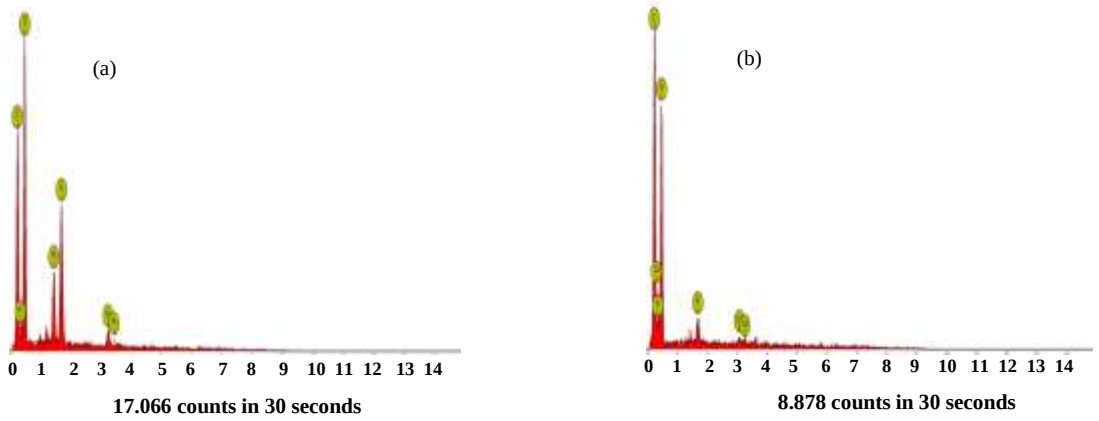

Fig. 7: EDS of blends of Henna with chitosan microparticles [before (a) and after (b) adsorption].

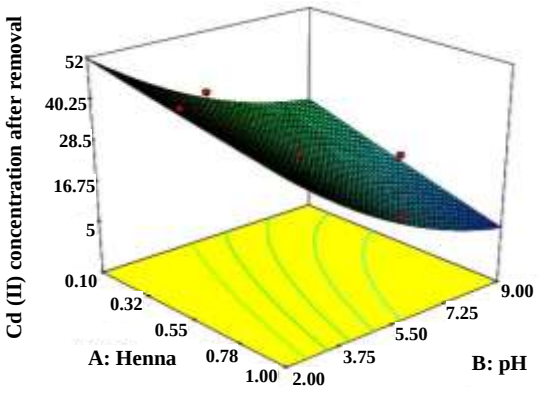

Fig. 8: Effect of interaction between pH and Henna dosage (g) in the level of Cd (II) residual concentration (ppm) on Henna.

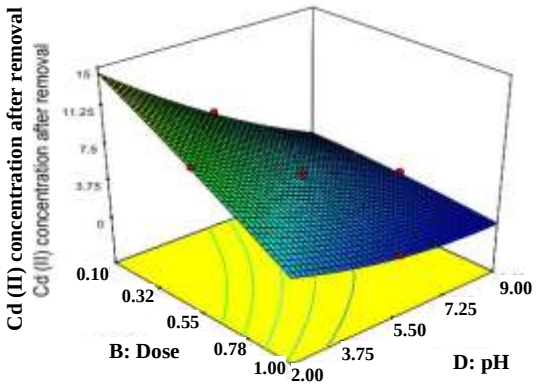

Fig. 9: Effect of interaction between pH and blends of Henna with chitosan microparticles dosage (g) in the level of Cd (II) residual concentration (ppm) on blends of Henna with chitosan microparticles.

conditions with heavy metal ions removal are less than 90 min [45-47]. According to the literature, the chitosan acquires a gel appearance at pH<3 and it cannot consider as an adsorbent while its solubility decreases with increasing pH up to 6. The chitosan solubility gradually increases at pH values higher than 7 while it remains constant at pH 8 and 9. Cadmium can react in solution with carbonates, phosphates, oxalates, arsenates, and cyanides depending on the pH of the solution, this element can also precipitate as hydroxide. Cadmium is mainly found as Cd^{2+} at pH≤8, and from this value up to pH 9 $Cd(OH)^{+}$ ions are formed [48]. Since these cations have a positive charge, they have recoiled from the solution at high pHs. Therefore, they are dramatically adsorbed on the adsorbents at maximum pH (before observing any sediment).

One of the main goals of this research was to find a model for the metal adsorption from a wastewater by a dried plant such as Henna and the Henna with chitosan microparticles. For this purpose, the isothermal models of Langmuir and Freundlich were applied to justify the adsorption process. The R^2 coefficient is a symbol of agreement between the experimental data and the modeled ones [45, 49]. Table 4 illustrates that R^2 in Freundlich isotherm is larger than that of the Langmuir one for both adsorbents. According to the Freundlich model, a suitable adsorbent has $0.2<1/n<0.8$ with high K_f, as well. Therefore, the Freundlich model legitimized Henna and the Henna with chitosan microparticles applications as strong adsorbents for heavy metals ions adsorption. Figs. 14(a-d) respectively show Cd (II) adsorption on the Henna based on the Freundlich and Langmuir models

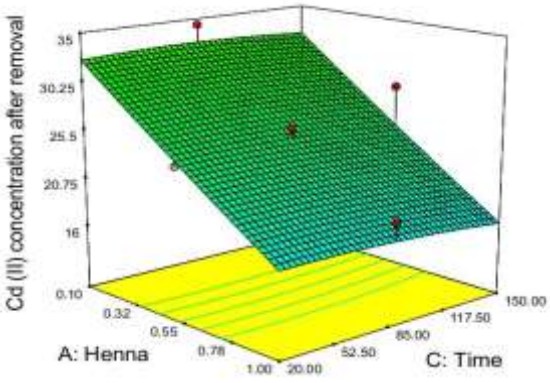

Fig. 10 Effect of interaction between Henna dosage (g) and time (min) in the level of Cd (II) residual concentration (ppm) on Henna.

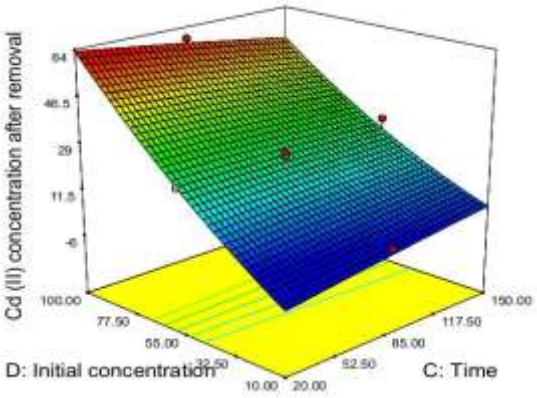

Fig. 12: Effect of interaction between initial concentration of the solution (ppm) and time (min) in the level of Cd (II) residual concentration (ppm) on Henna.

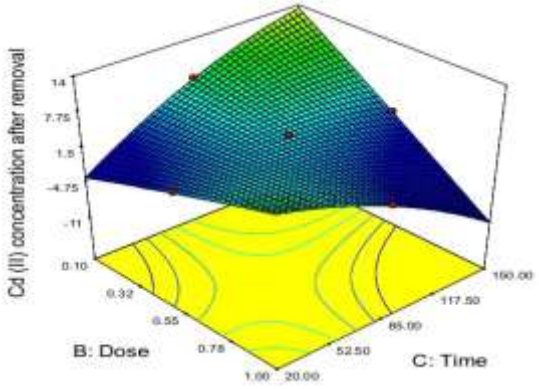

Fig. 11: Effect of interaction between blends of Henna with chitosan microparticles dosage (g) and time (min) in the level of Cd (II) residual concentration (ppm) on blends of Henna with chitosan microparticles.

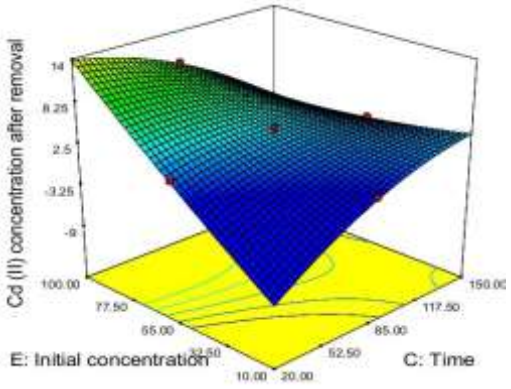

Fig. 13: Effect of interaction between initial concentration of the solution (ppm) and time (min) in the level of Cd (II) residual concentration (ppm) on blends of Henna with chitosan microparticles.

as well as Cd (II) adsorption on the blends of Henna with chitosan microparticles based on the Freundlich and Langmuir models. According to these figures, the Freundlich model properly illustrates Cd (II) adsorption on the Henna and blends of Henna with chitosan microparticles (with excellent R^2 data).

CONCLUSIONS

The main objective of this research was to find a cheap and abundant adsorbent such as Henna for Cd (II) adsorption from the aqueous wastewaters. Then, its quality was modified with low amounts of a fantastic adsorbent such as chitosan. This work was statistically designed and tested through experiments. Some correlations and operating conditions were found for scaling up in industries. The various isotherm models such as Langmuir and Freundlich ones were tested and validated in this research. The CCD (under RSM) conducted to study the effects of four adsorption parameters for pure Henna including time, initial concentration of Cd (II), Henna dosage and pH of solution and five parameters for the Henna with chitosan microparticles including time, initial concentration of Cd (II), Henna dosage, chitosan dosage and pH of solution. A second-order polynomial regression model could properly model the experiment with the R^2 of 0.9498 (F-value of 8.11) for Henna and 0.9988 (F-value of 213) for the Henna with chitosan microparticles. The data

Table 4: Adsorption isotherms parameters.

	Adsorbent	Langmuir	Freundlich
Diagram		C_e/q_e vs. C_e	*ln* C_e *vs. ln* q_e
The appropriate model	Henna	C_e/q_e =0.7635 + 0.0594 C_e	ln q_e =0.6975 + 0.4874 ln C_e
	Blends of Henna with chitosan microparticles	C_e/q_e = 0.2366+ 0.0419 C_e	ln q_e = 1.2482 + 0.6726 ln C_e
R^2 level	Henna	0.975	0.9949
	Blends of Henna with chitosan microparticles	0.8538	0.9955
The amount of equation parameters	Henna	q_{max} = 16.835	1/n= 0.4874
		b= 0.0777	K_f = 2.0087
	Blends of Henna with chitosan microparticles	q_{max} = 23.866	1/n = 0.6726
		b= 0.177	K_f = 3.484

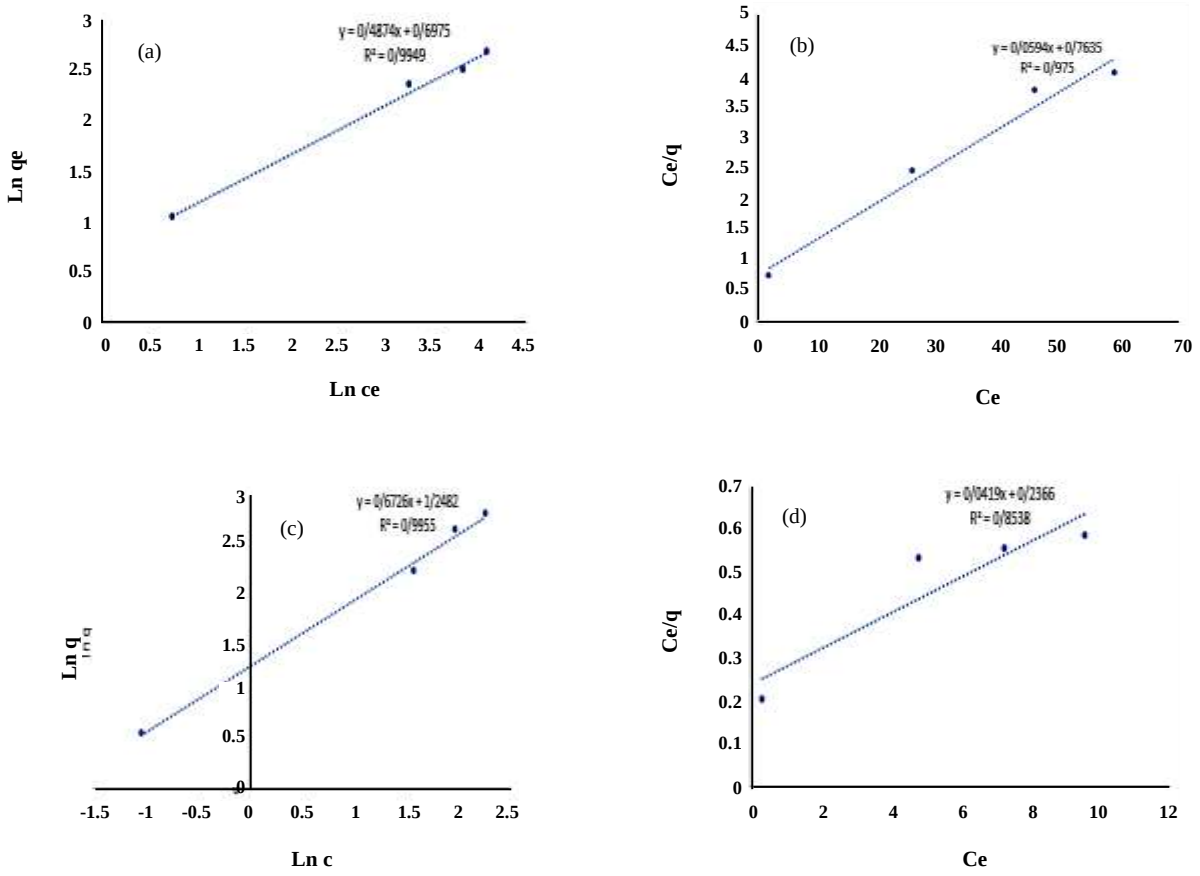

Fig. 14: Cd (II) adsorption on the Henna based on the Freundlich (a) and Langmuir (b) isotherm models as well as Cd (II) adsorption on the blends of Henna with chitosan microparticles based on the Freundlich (c) and Langmuir (d) isotherm models.

were in good agreement with both Langmuir and Freundlich isotherms. Furthermore, the obtained results showed that both adsorbents are suitable for the Cd (II) removal although the Henna with chitosan microparticles has fantastic quality in the Cd (II) removal.

Acknowledgement

This research was financially supported by Arak University (grant no.: 95/153 & date: 2016/4/26).

Received : Aug. 1, 2017 ; Accepted : Apr. 23, 2018

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