Application of response surface methodology for optimization of cadmium removal by Aloe Vera/carboxylated carbon nanotubes nanocomposite-based low-cost adsorbent

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Abstract

In this research, Aloe Vera leaf powder (OAMP) was modified with carboxylated carbon nanotubes (CNTs-COOH) and the prepared nanocomposite was used as a novel low cost adsorbent for the removal of cadmium ions from aqueous solutions. The prepared OAMP/CNTs-COOH nanocomposite was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Energy-dispersive x-ray spectroscopy (EDS) and Brunauer–Emmett–Teller (BET) analysis. The influence of operation parameters such as initial concentration of adsorbate, adsorbent dosage, contact time and pH of the cadmium solution on the cadmium adsorption process was studied by response surface methodology (RSM) optimization. The solid phase extraction (SPE) using OAMP/CNTs-COOH based-adsorbent was performed for the pre-concentration and matrix separation and inductively coupled plasma–mass spectrometry (ICP-MS) detector was used for measurement of cadmium ions concentration. The empirical adsorption data were fitted by Langmuir isotherm model. The value of maximum adsorption capacity was 46.95 mg g⁻¹, indicating high efficiency of OAMP/CNTs-COOH nanocomposite in the adsorption process of Cd(II). The kinetic of the Cd(II) adsorption process was followed by Elovich kinetic model. The reported thermodynamic parameters designated that the adsorption of Cd(II) on the OAMP/CNTs-COOH was an endothermic and spontaneous process. The results revealed that OAMP/CNTs-COOH demonstrate enhanced adsorption performance in comparison with non-treated Aloe Vera.

1. Introduction

In the recent times, the levels of environmental pollutants have increased to more than 4000 times of their initial values [1]. One of the most important sources of soil and water contamination is the release of heavy metals into the environment by various industries [2]. The most important source of pollution in the wastewater of some of the industries such as electrolyzing and electroplating industries, alloys, coating, batteries and pigments industries is the entry of heavy metal ions especially cadmium ions (Cd(II)) into the environmental waters [3]. Due to long biological half-life, high eco-toxicity, bioaccumulation, and non-degradability, presence of Cd(II) ions in water, even at the trace levels, has toxic effects on public health and the eco-system. Accumulation of Cd(II) ions in different tissues of the human body may cause serious damage such as broken bones, liver, kidney and lung cancer, negative effects on the respiratory system and high blood pressure [4]. Maximum contaminant level (MCL) of Cd (II) in drinking water has been reported about 3.0 μg l⁻¹ by the World Health Organization (WHO). Therefore, efficient and reliable treatment is required for the removal of cadmium ions from the industrial wastewaters and the environmental waters.
Various treatment methods have been used for the removal of heavy metal ions from aqueous solutions. Physicochemical deposition, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, solvent extraction, transfer methods, electrochemical oxidation and adsorption are the most common methods used for this purpose [5–7]. In the recent years, the adsorption method has received more attention due to high efficiency, low cost, easy manipulation and suitable applicability for the removal of the pollutants types [8]. Up to date, the types of different adsorbents like orange tree leaves [9], Burmese grape leaf [10], Clay-biochar Composite [11], rice husk [12], layered double hydroxides [13], poly (acrylic acid) activated carbon nanocomposite [14], \( \text{Al}_2\text{O}_3/ \)carbon composites [15], Carbon nanotubes [16], reduced graphene oxide [17] have been used for the removal purposes of cadmium ions. Using of Aloe Vera leaves and nano-adsorbents made from its leaves for the removal of pollutants from the aquatic environment have already been reported [18, 19].

Designing a new adsorbent based on Aloe Vera leaves waste for removal of heavy metal ions and especially cadmium ions from polluted water can be an efficient, uncomplicated and inexpensive route. To develop a more efficient adsorbent based on Aloe Vera, nanomaterial incorporation into pristine Aloe Vera can be a suitable approach in water treatment studies [20, 21]. Among various nanomaterials, carbon nanotubes (CNTs) could be potential candidates for adsorption purposes due to high specific surface area, unique structure, excellent thermal and mechanical resistance, and good flexibility during nanocomposites preparation [22, 23]. However, because of van der Waals interactions (\(\pi-\pi\) interactions), CNT based-adsorbents tend to agglomerate into bundles. Then practical usage of CNT based-adsorbents for achieving the high adsorption capacities is limited. The activation of carbon nanotubes with chemical reagents is a common method for increasing the hydrophilicity and decreasing the self-agglomeration of these adsorbents. Among various activation routes utilized for treatment of CNTs, chemical oxidation using strong inorganic acids can create various oxygen functions such as carboxyl and hydroxyl groups on the surface of CNTs [24]. Restrictions on the use of nanotubes due to their high cost has led researchers to use very little of it in making nanocomposite materials from inexpensive raw materials.

In this research, designing of an Aloe Vera based-novel potential nano-adsorbent by incorporation of the carboxylated carbon nanotubes into the pristine Aloe Vera (OAMP/CNTs-COOH) was our main purpose. The as-prepared nanocomposite based-adsorbent was characterized by FTIR, SEM, EDS and BET. The effective parameters in the adsorption process of cadmium ions onto OAMP/CNTs-COOH were optimized using response surface methodology.

The inductively coupled plasma–mass spectrometry instrument was utilized as detector. The kinetic and equilibrium of adsorption process of \(\text{Cd} \) (II) were evaluated by various isotherm and kinetic models. Langmuir isotherm and Elovich kinetic models were fitted well with experimental data of \(\text{Cd} \) (II) removal. Finally, the thermodynamic parameters of adsorption process including free Gibbs energy, enthalpy and entropy were determined. However, OAMP/CNTs-COOH nano-adsorbent offers promising futures in the removal of pollutants due to low cost, easy fabrication, environmentally friendly and stability in aqueous solutions.

2. Material and methods

2.1. Chemicals and instruments

2.1.1. Chemicals

Multi-walled carbon nanotubes (MWCNTs) with purity of more than 95 wt.%, diameter of 10–20 nm, and length of about 30 \(\mu\)m were purchased from Neutrino Company (Tehran, Iran). Sulfuric acid, nitric acid, cadmium nitrate, sodium hydroxide, hydrochloric acid and other chemical reagents were obtained from Merck Company and used without any purification. The Aloe Vera powder was prepared from the Aloe Vera plant grown in Bushehr (Iran). In all experiments, double distilled water was used for preparation of solutions.

2.1.2. Instruments

The Bruker Vertex 80 FT-IR spectrometer was used to determine the FT-IR spectra of prepared adsorbents of OAMP and OAMP/CNTs-COOH. To investigate the size and morphology of the prepared adsorbents, FESEM images were obtained using the SIGMA VP field emission scanning electron microscope furnished with EDS analyzer system. The \(\text{N}_2\) adsorption-desorption isotherms of the adsorbents were studied by using a quantum micrometer, Nova USA 3000, and the specific surface area, pore-volume, and mean diameter of the permanent cavities were calculated by BET and BJH analysis techniques. Hettich centrifuge (D-7200 Tuttilingen) was used to separate the solid particles of adsorbent from the solution containing cadmium ions. The cadmium concentration was measured by ICP-MS detector (Agilent, USA). The pH of the sample solutions was measured using a digital pH meter (SBP-11 Sartorius). The weight of the required solids was determined by LA/S analytical balance (LA 120 S, Germany). The Julabo MPH-5 thermostat manufactured by Julabo (Germany) was used for control of temperature. The prepared samples were dehydrated in an oven (Shimaz Co., Iran) for 24 h.
2.2. Preparation of adsorbent (OAMP/CNTs-COOH)

2.2.1. Preparation of powdered Aloe Vera
At first, the Aloe Vera gels were carefully removed from the Aloe Vera leaves. Then, the shanks and leaves were washed several times with distilled water and ethanol and dried in an oven at 40 °C for 1 h. The dried parts of Aloe Vera were crushed, powdered and sieved using 200 mesh sieve. The final micro powder of Aloe Vera was nominated as OAMP.

2.2.2. Preparation of carboxylated multi-walled carbon nanotubes
First, 0.5 g of MWCNTs was mixed with 50 ml of the mixture of concentrated sulfuric acid and nitric acid (in ratio of 3:1 v/v) and the resulting solution was refluxed at 70 °C for 5 h. Then, the resulted suspension was diluted with double distilled water and centrifuged at 6000 rpm for 30 min. The supernatant was discarded, and the precipitates were rinsed several times with double distilled water. The resulting precipitate (carboxylated carbon nanotubes) was dried in an oven at 100 °C for 24 h.

2.2.3. Preparation of Aloe Vera modified with carboxylated carbon nanotubes
0.05 g of carboxylated carbon nanotubes was added to 100 ml of deionized water and was stirred for 30 min. After this time, 1 g of OAMP was added to the suspension and was stirred at ambient temperature for 24 h. The suspension consisting of adsorbent phase was centrifuged (at 3500 rpm for 10 min) to separate sediment (adsorbent) from the solution. Finally, the obtained precipitate was washed with double distilled water for several times and dried in an oven at 70 °C for 24 h. To obtain fine and homogeneous particles, the prepared product was crushed, powered and sieved using a 200 mesh sieve. The prepared nanocomposite was nominated as OAMP/CNTs-COOH. The prepared adsorbents (OAMP and OAMP/CNTs-COOH) were characterized by FTIR, SEM, EDS as well as BET techniques.

2.2.4. Various loading of MWCNTs used in the structure of composite
In a simple experiment, various values of MWCNTs were mixed to constant value of OAMP adsorbent (1g). Then, under constant experimental conditions, cadmium ion adsorption test was performed using nanocomposites prepared with different amounts of MWCNTs. It was observed that with increasing the loadings of MWCNTs, the removal percentage increased (to 0.05 g), and with more increasing the loadings of MWCNTs, the removal percentage decreased (figure 1). Decreasing the percentage of removal with increasing the values of MWCNTs may be attributed to the accumulation of pipes. Based on these results, we chose 0.05 g MWCNTs as the suitable amount for preparing the composite with a good absorption percentage.

2.3. Adsorption experiments and the response surface methodology
In the present work, the response surface method (RSM) was applied to evaluate the performance of cadmium ions removal by prepared adsorbents using four independent variables. A Central Composite Design (CCD) was used to investigate the process using RSM in which a large number of experiments can be carried out in parallel and it is completely efficient in cases with up to five factors [25]. The number of experiments was obtained using the $2^k + 2k + C_p$ where $k$ is the number of factors, 2k points are in the corners of the cube showing the experimental domain, 2k axial points are in the center of each cube face and $C_p$ is the number of replicates in the center runs [26]. A CCD strategy allows a reasonable extent of information for examining the lack of fit, without

Figure 1. Various loadings of MWCNTs used in the structure of OAMP/CNTs-COOH nanocomposite.
involving a large number of design points [25]. A CCD with four independent variables including initial adsorbate concentration, adsorbent dosage, contact time and pH was used and removal efficiency of cadmium (II) ions (dependent variable) was considered as a response parameter. The results from the experiments designed by CCD were modeled via RSM which is suitable for correlating the second-order quadratic equations. The coded values of independent variables of Central composite design for Cd (II) removal are presented in table 1.

Outlier data points were removed from the model data prior to the final model analysis. Detection of outlier points was performed based on the calculation of the predicted residuals and the real values by the model. The curves obtained after removal of outliers data points by different methods are shown in figures 2(a)–(c) which points demonstrate that there is no outlier data point in the data matrix and all data are in the desired range.

Figure 2(d) shows the effect of each factor on the reaction (adsorption) efficiency. Three-dimensional response surface and contour graphs were drawn to illustrate the main and interactive effects of independent variables (figures 3(a)–(d)). According to the obtained surface diagrams, factor B (contact time) has a direct effect on the adsorption efficiency and the response increases with increase in the values of factor B. However, the response surface follows an upward trend with the other two factors, C (pH) and A (adsorbent dosage) and

### Table 1. Efficient parameters of Central composite design for Cd (II) removal.

| Name                | Units | Low  | High |
|---------------------|-------|------|------|
| Adsorbent dosing    | %w    | 0.01 | 0.03 |
| Cadmium concentration| mg l⁻¹ | 20   | 50   |
| Contact Time        | min   | 15   | 45   |
| pH                  | —     | 3    | 7    |

Figure 2. The plots of (a) predicted values versus actual ones, (b) residual values versus predicted ones after removal of outliers data points, (c) DFFITS versus run number after removal of outliers data points and (d) Perturbation diagram for comparing the effect of A, B, C and D factors on the response.
after reaching the maximum values, the trend decreases. In addition, the response values decrease with increasing factor D (concentration of cadmium ions).

The optimized values of the investigated factors are shown in figure 3(e). The optimal points of the factors (in red points) are proportional to the maximum response values.

The experimental data were analyzed and correlated well to the following second-order polynomial model [23] using Design Expert 8.0 software:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1 \neq j=1}^{k} \beta_{ij} X_i X_j + \epsilon$$

Where, $y$ is the predicted response; $X_i$ and $X_j$ are the input variables, $\beta_0$, $\beta_i$, $\beta_{ii}$ and $\beta_{ij}$ are the regression constants for intercept, linear, quadratic and interaction coefficients, respectively, and $\epsilon$ is the estimated error and $k$ is the number of variables. The statistical regression and graphical analysis of the obtained data were performed by Design-Expert software. In this analysis, the interactions between effective variables on the removal efficiency have been evaluated by the following quadratic polynomial equation:

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Figure 3. (a), (b) Response surface plots, (c), (d) contour plots for removal of cadmium ions from aqueous solution and (e) optimal values obtained for each effective factor.
Response\[68.88\&\;7.39\;A\&\;6.81\;B\&\;5.82\;C\&\;27.08\;D\&\;1.53\;AB\&\;1.54\;AC\&\;0.39\;AD\&\;3.16\;BC\&\;2.13\;BD\&\;2.65\;CD\&\;9.45\;A\&\;1.61\;B\&\;7.45\;C\&\;2222\]

Where A, B, C, and D represent the adsorbent dosage, the contact time, pH and the concentration of cadmium ions, respectively. The experimental results of Central Composite Design for the removal of Cd(II) ions from aqueous solution are presented in table 2. To display synergetic and antagonistic influences of the terms, positive and negative signs were used.

To evaluate the statistical analysis of the model, Analysis of variance (ANOVA) was utilized [27]. The summarized results of the ANOVA are given in table 3. The F-values and p-values (<0.05) demonstrated that the developed model is statistically significant [28]. Based on the results of ANOVA (table 3), the proposed model has sufficient reliability and accuracy for the prediction of cadmium ions adsorption onto the prepared adsorbent of OAMP/CNTs-COOH. The regression coefficient, which indicates the deviation of the experimental data from the proposed model, has been also estimated.

Here, F-values are used to compare the source mean squares with the residual mean squares which show the unexplained variations in the response. The lack of fit tells us whether a regression model is effective for predicting the empirical data or not. For a predictive model, the value of lack of fit should not be significant relative to the pure error (difference between replicate runs and the lack of appropriateness) indicating that this model is satisfactory and can be well correlated with the obtained results. The results of ANOVA Analysis for the response surface model are presented in table 3. According to this table, the p-value of the model is lower than 0.05 which indicates that the model is the significance and can predict the sample conditions to achieve the best absorption efficiency. The p-values of all linear terms for all factors (A, B, C, and D) are lower than 0.05, suggesting the significant effect of these parameters on adsorption efficiency. In addition, the interaction conditions are significant except for the interaction between the adsorbent dose and the cadmium concentration. Furthermore, it was also found that the quadratic terms rather than D^2 have significant effect on the adsorption efficiency. It is clear from the table that D factor (concentration of cadmium ions) with F-value of

| Run | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|-----|----------|----------|----------|----------|
|     | A: Adsorbent %w | B: Time min | C:pH | D: Conc ppm |
| 1   | 0.02     | 60.00    | 5.00    | 30.00    |
| 2   | 0.02     | 30.00    | 5.00    | 30.00    |
| 3   | 0.01     | 15.00    | 7.00    | 10.00    |
| 4   | 0.02     | 30.00    | 5.00    | 30.00    |
| 5   | 0.02     | 0.00     | 5.00    | 30.00    |
| 6   | 0.03     | 15.00    | 3.00    | 10.00    |
| 7   | 0.02     | 30.00    | 1.00    | 30.00    |
| 8   | 0.02     | 30.00    | 5.00    | 70.00    |
| 9   | 0.02     | 30.00    | 5.00    | 30.00    |
| 10  | 0.02     | 30.00    | 5.00    | 30.00    |
| 11  | 0.03     | 45.00    | 7.00    | 10.00    |
| 12  | 0.01     | 45.00    | 7.00    | 50.00    |
| 13  | 0.01     | 45.00    | 3.00    | 10.00    |
| 14  | 0.02     | 30.00    | 5.00    | 30.00    |
| 15  | 0.00     | 30.00    | 5.00    | 30.00    |
| 16  | 0.03     | 45.00    | 3.00    | 10.00    |
| 17  | 0.04     | 30.00    | 5.00    | 30.00    |
| 18  | 0.01     | 15.00    | 3.00    | 10.00    |
| 19  | 0.03     | 45.00    | 7.00    | 50.00    |
| 20  | 0.03     | 15.00    | 7.00    | 10.00    |
| 21  | 0.01     | 15.00    | 3.00    | 50.00    |
| 22  | 0.03     | 45.00    | 3.00    | 50.00    |
| 23  | 0.01     | 45.00    | 7.00    | 10.00    |
| 24  | 0.02     | 30.00    | 5.00    | 30.00    |
| 25  | 0.01     | 15.00    | 7.00    | 50.00    |
| 26  | 0.01     | 45.00    | 3.00    | 50.00    |
| 27  | 0.03     | 15.00    | 7.00    | 50.00    |
| 28  | 0.03     | 15.00    | 3.00    | 50.00    |
| 29  | 0.02     | 30.00    | 9.00    | 30.00    |
| 30  | 0.02     | 30.00    | 5.00    | 30.00    |
3723.99 has the most significant effect on the response (adsorption). The correlation coefficient of the model is higher than 0.9 indicating satisfactory predictive capability of the model. The adequacy value of the parameter or criterion of the signal-to-noise ratio is 69.8473, which indicates that the analytical signals require noise intensity to create and predict the model.

In the CCD method, first the effect of the factors affecting the process is identified and then the reaction conditions (adsorption) are maximized so that the response to the analysis (cadmium detection level) is maximized.

2.4. General description of the experiment
Inductively coupled plasma-mass spectroscopy (ICP-MS) technique was utilized to measure cadmium ions concentration in the samples and the CCD method was used to design the experiment. In the CCD method, first the effect of the factors affecting the process is identified and then the adsorption conditions are optimized to maximize the response for the analyte (cadmium detection level). Then, the range and level of variables as well as the conditions of each experiment are designed using appropriate software. The optimized levels of factors predicted by the model include adsorbent dose: 0.02 g, contact time: 30.45 min, pH: 6.37 and initial concentration of cadmium: 10.69 mg l\(^{-1}\). The procedure of the adsorption measurement was as follows: First, stock solution of cadmium (II) ions at concentration of 1000 mg l\(^{-1}\) was prepared by weighing and dissolving the corresponding compound in double distilled water. The working solutions of cadmium (II) ions were prepared by dilution of stock solutions with double distilled water to obtain known concentration (10–70 mg l\(^{-1}\)). The samples were analyzed with ICP-MS method and the results were used for plotting the calibration curve. According to the optimal conditions obtained from theoretical design, 100 ml of a solution containing cadmium (II) ions at concentration of 1000 mg l\(^{-1}\) was prepared by weighing and dissolving the corresponding compound in double distilled water. The working solutions of cadmium (II) ions were prepared by dilution of stock solutions with double distilled water to obtain known concentration (10–70 mg l\(^{-1}\)). The samples were analyzed with ICP-MS method and the results were used for plotting the calibration curve.

According to the optimal conditions obtained from theoretical design, 100 ml of a solution containing cadmium (II) ions at concentration of 1000 mg l\(^{-1}\) was prepared by weighing and dissolving the corresponding compound in double distilled water. The working solutions of cadmium (II) ions were prepared by dilution of stock solutions with double distilled water to obtain known concentration (10–70 mg l\(^{-1}\)). The samples were analyzed with ICP-MS method and the results were used for plotting the calibration curve.

After this time, the mixture was filtered with high-quality filter paper and cadmium (II) ions concentration was measured using ICP-MS. Using the initial concentration and the final concentration obtained after the experiment, the percentage of removal can be calculated according to the following equation:

\[
\text{percentage of removal} = \left(1 - \frac{C_e}{C_0}\right) \times 100
\]  

Where \(C_0\) and \(C_e\) are the initial and equilibrium concentration of cadmium ions in mg l\(^{-1}\) unit before and after the adsorption process, respectively.

| Source | Sum of Squares | d.f. | Mean Square | F-Value | p-value Prob > F |
|--------|----------------|-----|-------------|---------|-----------------|
| Model  | 14 621.89      | 13  | 1124.76     | 476.04  | <0.0001         |
| A-Con  | 582.14         | 1   | 582.14      | 246.38  | <0.0001         |
| B-Time | 494.32         | 1   | 494.32      | 209.21  | <0.0001         |
| C-pH   | 406.93         | 1   | 406.93      | 172.23  | <0.0001         |
| D-Con  | 7898.83        | 1   | 7898.83     | 3723.99 | <0.0001         |
| AB     | 28.15          | 1   | 28.15       | 11.91   | 0.0073          |
| AC     | 25.22          | 1   | 25.22       | 10.67   | 0.0097          |
| AD     | 1.60           | 1   | 1.60        | 0.68    | 0.4316          |
| BC     | 106.68         | 1   | 106.68      | 45.15   | <0.0001         |
| BD     | 48.31          | 1   | 48.31       | 20.33   | 0.0014          |
| CD     | 84.38          | 1   | 84.38       | 35.71   | 0.0002          |
| A\(^2\) | 314.60         | 1   | 314.60      | 133.15  | <0.0001         |
| B\(^2\) | 26.78          | 1   | 26.78       | 11.34   | 0.0083          |
| C\(^2\) | 887.91         | 1   | 887.91      | 375.80  | <0.0001         |
| D\(^2\) | 0              | 1   | 0           | 0.68    | 0.4316          |

Residual 21.26 9 2.36
Lack of Fit 2.68 3 0.89 0.29 0.8324
Pure Error 18.58 6 3.10
3. Results and discussion

3.1. Characterization of OAMP/CNTs-COOH bed-nanocomposite

The FTIR spectra provide important information on the chemical composition of CNTs-COOH and the prepared nanocomposite of OAMP/CNTs-COOH in the wavenumber range of 500–4000 cm\(^{-1}\) (figures 4(a) and (b)). For comparison, the spectrum corresponding to the OAMP was presented in figure S1 is available online at stacks.iop.org/MRX/7/065015/mmedia.

In the case of carboxylated MWNTs, the peak at 3436 cm\(^{-1}\) is characteristic of the stretching of hydroxyl group which can be related to the carboxyl groups or adsorbed water molecules on CNTs. The band at 1093 cm\(^{-1}\) assigned to the stretching vibration of C–O. The peak at 1727 cm\(^{-1}\), corresponded to the stretching mode of carboxylic groups in the structure of the acid-treated MMWNTs indicating that carboxylic groups are successfully introduced to CNT surface by chemical oxidation process. Appeared peak at 1634 cm\(^{-1}\) can be attributed to symmetric stretching of aromatic C=C bonds that is related to graphitic domains of CNTs. Also, peaks in around of 2924 cm\(^{-1}\) related to asymmetric stretching of CH\(_2\) groups were shown in the structure CNTs\(^{\text{29–31}}\).

The peaks at 3246 cm\(^{-1}\) and 2924 cm\(^{-1}\) can be attributed to the O–H and C–H stretching vibration of OAMP structure, respectively (figure S1). Two absorption peaks in around of 1630 cm\(^{-1}\) and 1432 cm\(^{-1}\), were also detected for the asymmetrical and symmetrical stretching of carboxylic acid (–COOH) groups\(^{\text{32}}\). The bands at 1248 cm\(^{-1}\) and 1320 cm\(^{-1}\) were also appeared due to the presence of C–O–C groups and O–H deformation, respectively\(^{\text{33}}\). The strong absorption peak at 1021 cm\(^{-1}\) assigned to the symmetric stretching

| adsorbent     | % C  | % O  | % Ca |
|---------------|------|------|------|
| OAMP          | 46.85| 48.45| 2.17 |
| OAMP/CNTs-COOH| 56.39| 40.92| 2.69 |

Figure 4. (a) FTIR spectrum of CNTs-COOH, (b) FTIR spectrum of OAMP/CNTs-COOH, (c) SEM image of CNTs-COOH, (d) SEM image of OAMP/CNTs-COOH and (E) elemental analysis of composite material of OAMP/CNTs-COOH with the percentage of elements of both adsorbents.
vibration of COO\(^{-}\) in the composition of OAMP. The peaks below 800 cm\(^{-1}\) are associated with metal-oxygen binding due to the presence of some metals in the composition of OAMP.

However, OAMP/CNTs-COOH nanocomposite showed similar IR peaks to both components of OAMP and CNTs-COOH (figure 4(b)). The presence of some shifts in position of the observed peaks along with their intensities reveals the existence of interaction among the components.

The surface morphology of the prepared samples was investigated by SEM images. SEM image of OAMP sample shows a sheet-like morphology with aggregated sheets (figure S2). Preserving their original shapes, creation of functional groups and reduction of re-stacking of carbon nanotubes on each other can be resulted from figure 4(c). However, in the case of OAMP/CNTs-COOH nanocomposite, the SEM image was completely different from single components (4d). The good dispersion of functionalized carbon nanotubes in OAMP structure can lead to an increase in the specific surface area of the composite, resulting in better adsorption of various organic analytes or heavy metal ions. Another issue which could be pointed out from the SEM images is that carbon nanotubes dispersed in composite material make it very difficult to detect nanotubes due to their high binding affinity among components as evidenced by IR study (shifts of IR peaks along with alteration of their intensities) further revealed the successful combination of two components.

The chemical composition of the OAMP/CNTs-COOH nanocomposite material was investigated by technique of EDS elemental analysis. The EDS spectrum for OAMP/CNTs-COOH nanocomposite is shown in figure 4(e) which shows the presence of carbon, oxygen, iron and cobalt in the composite material.

To investigate the surface area, porosity and total pore volume of samples, BET isotherms of OAMP/CNTs-COOH and OAMP samples were recorded. However, results revealed several characteristics of adsorbents, such as:

The Brunauer–Emmett–Teller (BET) surface area, pore diameter and total pore volume (determined from the Barrett–Joyner–Halenda (BJH) distribution curves) for the pure sample of OAMP were estimated to be 0.94 m\(^2\) g\(^{-1}\), 18.16 nm and 0.004 cm\(^3\) g\(^{-1}\), respectively.

The introduction of MWNTs-COOH into the OAMP results in a dramatic increase of specific surface area to 14.34 m\(^2\) g\(^{-1}\) which is very higher than that of OAMP sample.

Total pore volume of 0.080 cm\(^3\) g\(^{-1}\) and mean pore size of 22.4 nm was obtained for OAMP/CNTs-COOH nanocomposite.

It can be stated that despite the use of low levels of CNTs-COOH in nanocomposite preparation, the reason for high specific surface area of OAMP/CNTs-COOH nanocomposite is the good distribution of functionalized carbon nanotubes in OAMP sheets. In addition, BJH analysis showed the presence of mesopores in OAMP and also nanocomposite materials, which can be useful for adsorption of various analytes.

Zeta potential measurements at different values of pH was performed by zeta potential analyzer (Zeta-DLS, Zetasizer model, England). The value of zeta potential in pH = 3, pH = 6 and pH = 8 was −3.96, −22.3 and −34.2 mV, respectively. Because of increasing trend of zeta potential negative values from pH = 3 to pH = 8, pH\(\text{pzc}\) for OAMP/CNTs-COOH nanocomposite was estimated to be before pH = 3. Before isoelectric point (pH\(^{\text{III}}\), the surface charge of adsorbent was positive and the adsorption capacity of Cd(II) ions was decreased due to electrostatic repulsion interaction between the positive charge ofCd(II) and positive charge of OAMP/CNTs-COOH surface. At pH > pH\(\text{pzc}\), the amounts of Cd(II) ions adsorbed onto OAMP/CNTs-COOH nanocomposite increased over the studied pH range but experienced a rapid rise at pH 6.0–7.0. At pH > pH = 8, hydroxyl groups of alkaline area can react to positive Cd(II) ions and the Cd(II) ion adsorption was decreased due to the formation of metal–hydroxide composite.

3.2. Isotherm models

Adsorption equilibrium data obtained in this study were examined by six isotherm models including Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Flory–Huggins, and Jovanovic.

3.2.1. Langmuir model

Langmuir model is related to monolayer adsorption of solute on adsorbent phase with constant energy of adsorption [34]. The linear equation of this model is as follows:

\[
\frac{1}{q_e} = \frac{1}{K_L q_m} \left(\frac{1}{C_e}\right) + \frac{1}{q_m}
\]

(4)

Where \(q_m\) is the maximum adsorption capacity of Langmuir monolayer (mg g\(^{-1}\)), \(K_L\) is Langmuir model constant (L mg\(^{-1}\)), \(q_e\) is the equilibrium adsorption capacity (mg g\(^{-1}\)) and \(C_e\) is the equilibrium adsorbate concentration (mg L\(^{-1}\)). The values of \(\frac{1}{q_e}\) was plotted versus \(\frac{1}{C_e}\) (figure 5(a)) that results in line with slope of \(\frac{1}{K_L \times q_m}\) and intercept of \(\frac{1}{q_m}\). The calculated parameters from the different isotherms were listed in table 4.
Based on the obtained values for regression coefficient ($R^2$), it can be concluded that the Langmuir isotherm model ($0.9865$) is better than the other models for the description of the adsorption of cadmium ions onto the surface of OAMP/CNTs-COOH adsorbent. Also, the value of adsorption capacity evaluated from the Langmuir model ($50.25$ mg g$^{-1}$) is near to the experimental value. This value was higher than adsorption capacity of OAMP adsorbent sample ($9.5$ mg g$^{-1}$) at the same experiment conditions (data not shown here).

3.2.2. Freundlich model
Freundlich isotherm is based on multilayer sorption on a heterogeneous surface and its non-linear equation is expressed as follows [35]:

$$q_e = K_F C_e^{1/n}$$

(5)
Table 4. Various isotherm models and their parameters (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Jovanovic and Flory-Huggins) for the adsorption process of cadmium ions onto OAMP/CNTs-COOH adsorbent.

| Model                | Langmuir                  | Freundlich                  |
|----------------------|---------------------------|-----------------------------|
|                      | $q_m$ (mg g$^{-1}$)       | $N$                         |
|                      | 50.25                     | 8.33                        |
|                      | $K_L$ (l mg$^{-1}$)       | $K_F$ ($g^{-1}$/(1−1/n$_{FH}$)) |
|                      | 1.57                      | 3.34                        |
|                      | $R^2$                     | $R^2$                       |
|                      | 0.9865                    | 0.6201                      |

| Model                | Temkin                    | Dubinin–Radushkevich       |
|----------------------|---------------------------|-----------------------------|
|                      | $B_T$                     | $q_m^*$ (mg g$^{-1}$)       |
|                      | 4.136                     | 46.39                       |
|                      | $K_T$ (l mg$^{-1}$)       | $K_D$ (mol$^{-1}$)         |
|                      | 5180.76                   | $3 \times 10^{-8}$         |
|                      | $R^2$                     | $R^2$                       |
|                      | 0.5406                    | 0.8415                      |

| Model                | Jovanovich                | Flory-Huggins              |
|----------------------|---------------------------|-----------------------------|
|                      | $q_m$ (mg g$^{-1}$)       | $n_{FH}$                   |
|                      | $K_J$ (l mg$^{-1}$)       | $K_{FH}$ (mg$^{-1}$)       |
|                      | $R^2$                     | $R^2$                       |
|                      | −17.968                   | −0.7197                     |
|                      | −0.08                     | 0.0074                      |
|                      | 0.1769                    | 0.9000                      |

The linearized form of the above equation can be rewritten as:

$$\ln q_e = \ln K_T + \frac{1}{n} \ln C_e$$

(6)

Where $K_T$ (l mg$^{-1}$) is Freundlich constant that is related to the surface heterogeneity and $n$ is another constant of this model. The parameters of $q_m$ and $C_e$ are the same as the Langmuir model. In this model, values of $\ln q_e$ were plotted against $\ln C_e$ (figure 5(b)) and the evaluated constants of Freundlich model were presented in table 4. The obtained value for $R^2$ was 0.6021, indicating that this model is not suitable for describing the adsorption process in comparison to the Langmuir isotherm model.

3.2.3. Temkin model

In the isotherm model of Temkin [36], the effect of the interactions of adsorbate/adsorbent on the adsorption process is considered. Moreover, it was assumed that the adsorption heat of all species in the layer declines linearly by increasing the surface coverage.

$$q_e = B_T \ln C_e + B_T \ln K_T$$

(7)

where $K_T$ (l mg$^{-1}$) is the Temkin isotherm constant indicating the affinity of adsorption and $B_T$ (mg g$^{-1}$) corresponds to the heat of adsorption. With drawing of plot of $q_e$ versus $\ln C_e$, the parameters of this model was obtained and presented in (figure 5(c)) and table 4. According to the obtained value for $R^2$ (0.5406), it is concluded that the Temkin model is also not suitable for correlating the adsorption data.

3.2.4. Dubinin–Radushkevich model

Dubinin–Radushkevich isotherm model [37] is usually used to describe adsorption process with Gaussian energy distribution onto heterogeneous surfaces. The linear equation of this model is as follows:

$$\ln q_e = -K_{DR} \varepsilon^2 + \ln q_m$$

(8)

Where $q_m$ is Dubinin-Radushkevich maximum adsorption capacity (mg g$^{-1}$), $\varepsilon$ is Polanyi potential (kJ mol$^{-1}$) and $K_{DR}$ is isotherm constant (mol$^{-1}$ kJ$^{-1}$) obtained from the free energy of adsorption, $E$ (kJ mol$^{-1}$) can be calculated according to the following equation:

$$E = \frac{1}{(2K_{DR})^{0.5}}$$

(9)

Drawing a $\ln q_e$ plot against $\varepsilon^2$ based on the Dubinin–Radushkevich isotherm model results in a straight line with slope of $-K_{DR}$ and intersection of $\ln q_m$ (figure 5(d)). The parameters of this isotherm model were given in table 4. According to the obtained value for $R^2$ (0.841), it can be said that this isotherm is not appropriate for describing the adsorption process.

3.2.5. Jovanovich isotherm

This model has been derived based on the assumptions used in the Langmuir model but it also includes the possibility of some mechanical contacts among the adsorbate and adsorbent phase. The linear form of this model is [38, 39]:

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**Table 4.** Various isotherm models and their parameters (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Jovanovic and Flory-Huggins) for the adsorption process of cadmium ions onto OAMP/CNTs-COOH adsorbent.
Where $q_e$, $q_m$, and $K_J$ are the equilibrium adsorption capacity (mg g$^{-1}$), maximum adsorption capacity (mg g$^{-1}$) and Jovanovic isotherm constant (lg g$^{-1}$), respectively. The evaluated parameters of the Jovanovic model are presented in Table 4. The values of $q_e$ were plotted versus $C_0$ and presented in Figure 4(e). The linearized equation results in correlation coefficient of $R^2 = 0.176$, which designates that the Jovanovic model is very unsuitable for prediction of the experimental adsorption data.

### 3.2.6. Flory–Huggins isotherm

This isotherm model describes the surface coverage of the adsorbent by the adsorbate molecules or ions. The linear equation of this model is expressed as follows [40]:

$$\ln q_e = \ln q_m + K_{FH} \ln q_m$$  \hspace{1cm} (10)

Where $q_e$, $q_m$, and $K_{FH}$ are the equilibrium adsorption capacity (mg g$^{-1}$), maximum adsorption capacity (mg g$^{-1}$) and Flory-Huggins isotherm constant (1 g$^{-1}$), respectively. The evaluated parameters of the Flory-Huggins model are presented in Table 4. The values of $q_e$ were plotted versus $1 - \frac{C_e}{C_0}$ and presented in Figure 4(e). The linearized equation results in correlation coefficient of $R^2 = 0.176$, which designates that the Flory-Huggins model is very unsuitable for prediction of the experimental adsorption data.

### Table 5. Comparison of the adsorption capacities of Cd(II) ions for various adsorbents.

| Adsorbent                                           | pH  | $q_m$ (mg g$^{-1}$) | References |
|-----------------------------------------------------|-----|---------------------|------------|
| Disulfide linked polymer networks (COP63)           | 6.0–8.0 | 9.9 | [41] |
| oxygen-doped carbon nitride                         | 6.0 | 33.9 | [42] |
| PVA-immobilized Aspergillus niger                   | 5.5 | 60.24 | [43] |
| natural phosphate (NP)                              | 5.0 | 26 | [44] |
| Novel biopolymer-coated hydroxyapatite foams        | 2.0 | 35.52 | [45] |
| Moroccan stevensite                                 | 7.0 | 22.37 | [46] |
| Impregnated Styrofoam                               | 6.0–8.0 | 29.11 | [47] |
| Multiwall carbon nanotubes                          | 3.0 | 4.5 | [48] |
| Dried cactus (Opuntia ficusindica) cladodes         | 3.5, 5.8 | 30.42 | [49] |
| OAMP/CNT-COOH                                       | 6.37 | 46.95 | This work |

In this equation, $\theta$ is the degree of surface coverage, $n_{FH}$ and $K_{FH}$ are Flory-Huggins’s constants that defined as the number of ions adsorbed on the adsorption sites and the equilibrium constant of adsorption, respectively. Slope and intercept of $\ln \left( \frac{q_e}{C_0} \right)$ plot against $\ln \left( 1 - \frac{C_e}{C_0} \right)$ are $n_{FH}$ and $\ln K_{FH}$, respectively. The results of this model can be seen in Table 5 and the obtained value of $R^2$ (0.9000) shows that the Flory-Huggins model is a suitable model for description of the adsorption data. The appropriateness of the used models (in term of $R^2$) are as follows:

Langmuir > Flory–Huggins > Dubinin – Radushkevich > Freundlich > Temkin > Jovanovich.

The results confirmed that Langmuir isotherm model could be the most appropriate model in comparison to other isotherm models for fitting the experimental data. Also, it revealed that the adsorption of the cadmium ions on the surface of the OAMP/CNTs-COOH adsorbent was monolayer and all the active sites of adsorbent phase have equal affinity to cadmium ions.

The OAMP/CNTs-COOH adsorbent showed comparable or even better performance for Cd$^{2+}$ ions adsorption in comparison to the adsorption capacity of the other carbon-based materials or hybridized composites (Table 5). The low cost and simple synthesis route of the as-prepared nanocomposite make it as appealing candidate for effective removal of Cd (II) ions from aqueous solutions.

### 3.3. Adsorption kinetics

The adsorption process is a time-dependent process, so the kinetic study of adsorption can be useful to find out the adsorption pathways of cadmium ions on the surface of OAMP/CNTs-COOH adsorbent [50]. To describe the kinetic of adsorption process in the present study, several kinetic models including pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models were utilized.
3.3.1. Pseudo-first-order model

The linearized form of the equation of the pseudo-first-order kinetic model is given as follows [51]:

\[
\log(q_e - q_t) = -\frac{k_1}{2.303} t + \log q_e
\]  

(13)

Where \( q_e \) is the adsorption capacity at equilibrium (mg g\(^{-1}\)) and \( k_1 \) is the rate constant of the pseudo-first-order model (min\(^{-1}\)). As shown in figure 6(a), the values of \( \log(q_e - q_t) \) were plotted versus \( t \) and the obtained model parameters \( (k_1, q_e \text{ and } R^2) \) were listed in table 6. The slope and intercept of \( k_1/2.303 \) and \( \log q_e \) were attained from this linear relationship, respectively. The obtained value for \( R^2 \) was 0.7936.

3.3.2. Pseudo-second-order model

Pseudo-second-order model [52] assumes that the rate of adsorption is proportional to the square of the number of available sites for adsorption process. The linearized equation for the pseudo-second-order model is given as follows:
\[ \frac{t}{q_t} = \frac{t}{q_e} + \frac{t}{k_c q_e^2} \]  

(14)

where \( k_c \) is the rate constant of this model (g mg\(^{-1}\) min\(^{-1}\)). The \( \frac{t}{q_t} \) values were plotted versus \( t \) (figure 6(b)) and the resulted parameters of this equation were presented in table 6. Based on the calculated value of \( R^2 \) (0.5422), pseudo-second-order model can not be a suitable case for describing the adsorption kinetic.

3.3.3. Intraparticle diffusion

Adsorption is a multi-step process that involves the transfer of solute molecules from the aqueous phase to the surfaces of solid particles of adsorbent, which is confirmed by diffusion into the internal pores of adsorbent. The linearized equation for the Intraparticle diffusion model is presented as follows [53]:

\[ q_t = K_{\text{diff}} t^{1/2} + C \]  

(15)

Where \( q_t \) (mg g\(^{-1}\)), \( C \) and \( K_{\text{diff}} \) (mg g\(^{-1}\) min\(^{-1/2}\)) are the adsorption capacity in the required time for each experiment, thickness of the boundary layer (mg g\(^{-1}\)) and the Intraparticle diffusion rate constant, respectively. Plot of \( q_t \) versus \( t^{1/2} \) was presented in figure 6(c) and the obtained parameters of the intraparticle diffusion model were listed in table 6. The obtained value of \( R^2 \) is 0.9434 which means that this model is more suitable for the description of the adsorption kinetic in comparison to two previous mentioned kinetic models.

3.3.4. Elovich model

Elovich kinetic model is applied to describe heterogeneous adsorption energy over the adsorbent surface. The linearized form of this model is showed by following equation [54]:

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t) \]  

(16)

Where \( \beta \) is Elovich constant (g mg\(^{-1}\)) and is related to the amount of surface coverage and the activation energy for chemisorption and \( \alpha \) is the initial rate of adsorption process (mg g\(^{-1}\) min\(^{-1}\)). The model constants, \( \beta \) and \( \alpha \) were determined from the plot of \( q_t \) versus \( \ln(t) \) values (figure 6(d)) and listed in table 6. The value of \( R^2 \) is 0.9862 which indicates that this model is the best model among the other kinetic models for explanation of the kinetics data.

3.4. Estimation of the thermodynamic parameters

The thermodynamic parameters of the adsorption process such as enthalpy, Gibbs free energy, and entropy were determined by the following equation:

\[ \Delta G_{\text{ads}}^o = -RT \ln K_c \]  

(17)

\( K_c \) can be calculated from the following equation [55, 56]:

\[ K_c(T) = \frac{q_e}{C_e} \]  

(18)

Where \( q_e \) and \( C_e \) are equilibrium capacity of adsorbent and equilibrium concentration of the sorbate, respectively. The enthalpy changes (\( \Delta H_{\text{ads}}^o \)) and entropy changes (\( \Delta S_{\text{ads}}^o \)) for adsorption are assumed to be temperature independent [57, 58] and the Gibbs free energy changes (\( \Delta G_{\text{ads}}^o \)) is related to the enthalpy and entropy changes by the following equation:

\[ \Delta G_{\text{ads}}^o = \Delta H_{\text{ads}}^o - T \Delta S_{\text{ads}}^o \]  

(19)

A study on the dependence of the adsorption process on temperature gives valuable information about the changes in enthalpy and entropy during adsorption. The relationship between \( \ln K_c \) and \( T \) was shown in figure 7(a) in the form of a plot and the estimated adsorption thermodynamic parameters were listed in table 7.

According to the resulted data in table 7, the adsorption process is spontaneous due to the negative values of \( \Delta G_{\text{ads}} \). The positive values of \( \Delta H_{\text{ads}} \) and \( \Delta S_{\text{ads}} \) indicate the endothermic nature of adsorption process and increasing in the disorder. In addition, increasing the removal efficiency with increasing the temperature also indicates the physical absorption or endothermic nature of this process (figure 7(b)).

3.5. Separation factor

The dimensionless factor of \( R_t \) which can be used for determination of the nature of the adsorption process was estimated from the parameters of Langmuir equation (equation (7)).

After selecting Langmuir isotherm as the best isotherm model, the parameter of \( R_t \) was evaluated from equation (20) [59]:
Where \( C_0 \) is initial concentration and \( K_L \) is the constant related to the energy of adsorption (Langmuir Constant). Various amounts of RL have different interpretations. If \( R_L > 1 \), the adsorption is unfavorable, for RL values between 0 and 1, adsorption process is favourable and RL value equal to 1 reveals that the adsorption process is linear. The \( R_L \) values attained at various concentrations were between 0 and 1 (table 8). Accordingly, it is concluded that the Langmuir isotherm is appropriate and can explain the experimental results for the adsorption of cadmium ions from aqueous solutions by OAMP/CNTs-COOH adsorbent.

### 3.6. Reusability of adsorbent

To study the potential of OAMP/CNTs-COOH adsorbent for real usages, the reusability of the adsorbent was investigated by successive cycles. Some chemicals such as 0.1 M of HCL, NaOH and HNO3 were used with purpose of regenerating the adsorbent after Cd (II) ions adsorption, so the use of HNO3 yields the best results for reusability of the adsorbent [59].

Figure 8 exhibits the percentage change in the adsorption capacity of Cd (II) in ten repetitive cycles by HNO3 as desorption media. The results revealed that after five repetitive cycles, the adsorbent retains about 91.8% of its initial capacity for adsorption of Cd (II) ions from the aqueous solution. This study demonstrated the high performance and reusability of OAMP/CNTs-COOH adsorbent for cadmium ions removal. However, after ten adsorption cycles, adsorbent still retains 74.2% of its adsorption capacity. These results dedicate that the adsorption of Cd (II) ions by the nanocomposite occurred through complexation of Cd (II) ions with functional groups of the existence components in the composition of the adsorbent.

### Table 7. The values of thermodynamic parameters for the adsorption of cadmium ions onto OAMP/CNTs-COOH adsorbent.

| \( T \) (K) | \( \Delta G_{ads} \) (kJ.mol\(^{-1}\)) | \( \Delta H_{ads} \) (kJ.mol\(^{-1}\)) | \( \Delta S_{ads} \) (J.mol\(^{-1}\).K\(^{-1}\)) |
|---|---|---|---|
| 283 | -4.986 | | |
| 293 | -9.261 | | |
| 298 | -11.398 | +116 | +427 |
| 303 | -13.536 | | |

### Table 8. The values of \( R_L \) factor calculated for the adsorption process of cadmium ions onto OAMP/CNTs-COOH adsorbent.

| \( C_0 \) (mg.L\(^{-1}\)) | 10 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|
| \( R_L \) | 0.018 | 0.0091 | 0.0061 | 0.0046 | 0.0036 |

\[ R_L = \frac{1}{1 + K_L C_0} \]  

Where \( C_0 \) is initial concentration and \( K_L \) is the constant related to the energy of adsorption (Langmuir Constant). Various amounts of \( R_L \) have different interpretations. If \( R_L > 1 \), the adsorption is unfavorable, for \( R_L \) values between 0 and 1, adsorption process is favourable and \( R_L \) value equal to 1 reveals that the adsorption process is linear. The \( R_L \) values attained at various concentrations were between 0 and 1 (table 8). Accordingly, it is concluded that the Langmuir isotherm is appropriate and can explain the experimental results for the adsorption of cadmium ions from aqueous solutions by OAMP/CNTs-COOH adsorbent.

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4. Conclusion

Aloe Vera treated with carboxylated carbon nanotubes proved to be an eco-friendly, low cost and efficient new adsorbent for the removal of cadmium ions from wastewaters. The optimum adsorption conditions determined by response surface method were as: adsorption dose = 0.02 g, contact time = 30.45 min, pH = 6.37 and initial concentration of cadmium ions = 10.69 mg l\(^{-1}\). In the optimal condition, the adsorption percent of cadmium ions onto the OAMP/CNTs-COOH adsorbent reached to about 98%. Among various isotherms, Langmuir and Flory–Huggins models were followed for the adsorption of cadmium, with the calculated maximum adsorption capacity of 46.95 mg g\(^{-1}\). kinetic data of adsorption process were well described by the Elovich kinetic model. The calculated values of thermodynamic parameters showed that the adsorption process was endothermic and spontaneous. The calculated separation factor was between 0 and 1 which means that Langmuir isotherm is appropriate for description of the experimental results. The studies of reusability of adsorbent confirmed that prepared adsorbent retained about 74.2% of its capability after ten successive adsorption-desorption.

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Figure 8. Recovery yield of OAMP/CNTs-COOH adsorbent for Cd (II) adsorption after ten repetitive adsorption-desorption cycles.
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