

The Thermodynamic and Kinetics Study of Removal of Cd(II) by Nanoparticles of Cobalt Oxide in Aqueous Solution

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ABSTRACT: Cadmium is an extremely toxic metal, which even in low levels is harmful to the human body, animals and also plants. Human manufactures such as cadmium-nickel batteries and pesticides, plastic, make the earth polluted with cadmium; therefore removal of the cadmium Water is vital for human and animal. Scientists use different methods for cadmium removal including adsorption, precipitation, ion exchange, and solvent extraction. In this study the removal of cadmium ion from aqueous solution by nanoparticles of cobalt oxide were investigated. The sol-gel method was used to synthesize cobalt oxide nanoparticles. The characterization of synthesized cobalt oxide was investigated by Fourier Transfer Infrared Spectrometry (FT-IR), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM), and a Transmission Electron Microscope (TEM). The important parameters influencing on the adsorption process were studied, including pH, buffer volume, amount of adsorption, contact time, in-time differentiate temperature and Taguchi designed experiment. The kinetic of removal process was investigated and found that it is followed pseudo second-order kinetics. In this study, four famous isotherms were considered to investigate and the results indicated that the Langmuir model gave a better fit to the experimental data.

KEYWORDS: Cadmium; Removal; Isotherm model; Cobalt oxide.

INTRODUCTION

Cadmium can be found in the environment by the slow process of erosion and abrasion of rocks and soils. It can be generated by natural events such as volcanic eruptions or artificial events like textile operations, refining industries, pigments, dyes, and forest fires, etc. [1]. Cadmium like other metals resists and remains in nature for a long time. Because of this reason it attracts many attentions. Nevertheless, to solve heavy metal pollution in nature, it is crucial to bring applicable solutions or invent some new catalysts. Therefore,

the treatment or purification of contaminated environment and effluents is one of the major areas of active studies. World health organization's recommendation for Cd(II) maximum concentration in drinking water is 0.005 mg/L. Najafi and co-workers used synthesized NH₂-SG and NH₂-SNH to remove heavy metals such as cadmium [2]. For this method, their results revealed that the best association is Langmuir-Freunlich Isotherm adsorption model and the pseudo-second order for the kinetic model. Yang *et al.* investigated the adsorption Isotherms and also

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1021-9986/2019/1/127-139

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the kinetic of the reaction of cadmium removal by using TiO_2 as adsorbent [3]. Their result shows that the reaction has a pseudo-first order kinetic model and its adsorption isotherm follows the Langmuir model. *Hamidpour et al.* successfully used natural zeolite to remove $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ and they found that the process is very slowly reversible sorption [4]. They found that Zeolites have a great capability to remove heavy metals from the wastes. Adsorption capacity reported in this study is 1.179 mg/g and the efficiency is above 98 percent. *Ossman et al.* used a bundle of newspaper to remove cadmium ions [5]. They found that by increasing the pH cadmium removal will be more efficient. This removal is dramatically faster for 5 to 30 mg/L cadmium solution and it is about 15 minutes. *Younesi et al.* examined cementation of cadmium ions by zinc powder in a batch reactor at low and high concentrations at pH 5.2–5.4 and they show that the reaction is first-order kinetically [6]. They found that the deposited layer was metallic with no evidence of basic zinc sulphate or re-dissolution of cadmium. Marder and co-worker used the electro-dialysis technique for the treatment of synthetic waste water including approximately 0.0089 mol/L cadmium(II) ions and 0.081 mol/L cyanide using a five-compartment electro-dialysis cell [7]. *Hosseinzadeh et al.* explored the cadmium ion removal from the aqueous solution by using activated carbon produced by eroded tiers [8]. They found that cadmium removal will be better if the pH goes up. They found that the adsorption isotherm follows the Langmuir model and reported 83.33 mg/g for adsorption capacity. *Hizal and Apak* studied about cadmium adsorption on kaolinite-based clays in the absence and presence of humic acid and modeled with the aid of the FITEQL 3.2 computer program using a modified Langmuir approach for capacity calculations [9].

Many researches have been used nanotechnology in their study, recently *Soltani et al.* used amino-modified MCM-41/poly(vinyl alcohol) nanocomposite (M-MCM-41/PVOH NC) as a green adsorbent for removal of $\text{Cd}(\text{II})$ from aqueous solution [10]. Metal oxide nanoparticles, due to their conspicuous physicochemical properties, have attracted considerable attention in many fields. One significant approach is to use these nanoparticles in removing the heavy metals such as chromium, cadmium, and zinc. *Sheela et al.* applied zinc oxide nanoparticles to removal of Zn (II), Cd (II) and Hg (II) from aqueous

solution [11] and *Mahmoud et al.* used titanium oxide nanoparticles with chitosan nanolayer for instantaneous microwave sorption of $\text{Cu}(\text{II})$ and $\text{Cd}(\text{II})$ from water [12] and *Gupta et al.* prepared Fe_2O_3 nanoparticles with orange peel powder as a nano-adsorbent for cadmium ion removal [13]. Intensive researches on Cobalt Oxide nanoparticles has been done because of its applications in heterogeneous catalysis, gas sensors, Solar cells, Magnetic materials, and rechargeable batteries. The usefulness of adsorbents as an agent for removing heavy metals has been studied widely. *Zaman et al.* studied the effect of phosphate complexation on $\text{Cd}(\text{II})$ adsorption by manganese dioxide ($\beta\text{-MnO}_2$) [14]. They explored the adsorption properties of manganese dioxide in the presence of phosphate which is thought to be one of the most important complexes forming species. They show that $\text{Cd}(\text{II})$ adsorption increased with increasing pH, temperature and phosphate concentration. Also they show that phosphate formed both outer and inner sphere complexes via metal and ligand-like adsorption. The Langmuir equation was applied to describe the data and from the constants of this equation different thermodynamic parameters such as ΔH^0 , ΔS^0 and ΔG^0 were studied. *Mamata et al.* synthesized high surface area (176.16 m²/g) nano akaganeite ($\beta\text{-FeOOH}$) powder using 1M ferric chloride solution, 0.2M EDTA solution as the chelating agent and ammonia for neutralization [15]. They found that with the increase in pH from 2 to 5, uptake of metal ions is increased and the adsorption kinetics followed the pseudo-second order model. Both Langmuir and Freundlich models fitted well to the isothermic data. High loading capacities of 50 mg/g were obtained for $\text{Cd}(\text{II})$. *Sen and Sarzali* used synthetic Al_2O_3 to find out its adsorption capacity for the removal of cadmium(II) ions in solutions [16]. The kinetic study clearly indicated that adsorption of cadmium metal ion (Cd^{2+}) on aluminum oxide was a two steps process: very rapid adsorption of cadmium metal ion to the external surface is followed by possible slow intra-particle diffusion in the interior of the adsorbent. Overall the cadmium adsorption process followed pseudo-second-order kinetics.

The goal of this research study was to obtain the basic information to find the model of adsorption isotherm and the kinetic of the removal of cadmium (II) by cobalt oxide nanoparticles which is synthesized by the sol-gel method.

To obtain better performance and consequently knowing the particle's size and morphology of nanoparticles of cobalt oxide structure, the FT-IR, XRD, SEM and TEM techniques were used. The influence of pH, buffer volume, amount of adsorption, contact time, in-time differentiate temperature and Taguchi designed experiment were studied. The appropriate kinetical model was indicated. The obtained results might help to a better understanding of the adsorption phenomena for cadmium.

EXPERIMENTAL SECTION

All chemicals used in this research were of analytical grade. The chemicals used in the synthesis of nanoparticles of cobalt oxide were $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and oxalic. All the solutions were made in double distilled water.

Adsorbent

The Cobalt oxide nanoparticles were used in this study as adsorbent and there are many methods to synthesis the cobalt oxide nanoparticles. The sol-gel method was chosen to prepare the adsorbent because this method is fast and not expensive compare with the other method. In this method, first in one beaker the cobalt salt solution was mixed in double distilled water with continuous stirring for 1 hour. In another beaker oxalic acid solution was again prepared in double distilled water and continuous stirring for half an hour. The oxalic acid was then mixed into the cobalt salt solution drop wise with continuous stirring for three hours. The resultant light pink colored precipitates were washed with double distilled water and then dried at 100°C in an oven for 5 h. Finally, the obtained cobalt hydroxide was calcined in air for 4 h at 250°C , which was used to characterize as nanoparticle and as adsorbent in the removal process.

Adsorbate

The cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%, Merck, Germany) was used as the precursor salts for the cadmium (II) solution present in wastewater. An individual stock solution was prepared by dissolving a specified amount of the cadmium nitrate in 250mL of deionized water, and then diluted to the required concentrations. The cadmium salt was used without further purification.

In all adsorption experiments the necessary amount of prepared of cobalt oxide nanoparticles was taken

in a 250 mL conical flask containing 10 mL of desired concentration of the test solution for the batch adsorption studies at the desired pH value. The measurement of Cd(II) concentration was done by atomic absorbance spectrometer technique before and after the adsorption process.

RESULT AND DISCUSSIONS

Characterization

The synthesized adsorbent powder was used to characterize. First, the XRD technique was applied to find out the crystal structure and estimate the particles size. Then to discover the functional group in the structure the FTIR technique was used. By using the SEM and TEM techniques, the morphology and microstructure of adsorbent were investigated.

First XRD patterns of the Co_3O_4 nanoparticles powder which calcined at 250°C , is shown in Fig. 1, which indicates the cobalt oxide has a cubic phase structure. The peak positions at ($2\theta = 19.37^\circ, 31.57^\circ, 37.17^\circ, 45.09^\circ, 55.80^\circ, 59.65^\circ$ and 65.45°) and relative intensities obtained for the Co_3O_4 match with the JCPDS card No: 073 1701 file. There were no characteristic peaks of impurity were observed.

The average grain size of Co_3O_4 is determined by using the Scherrer equation crystallite size (1), and it was found to be 17.377 nm. According to Fig. 1 the maximum peak is at $2\theta = 3.17$ and the full width at half maximum (FWHM) is $\beta = 0.47$ therefore:

$$d = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

Where D is mean size of crystalline, λ is the x-ray wave length, β is the line broadening at half the maximum intensity ((FWHM) and θ is the Beragg angle.

$$2\theta = 3.17 \rightarrow \theta = 18.58$$

$$\cos(18.58) = 0.95$$

$$\lambda = 1.54 \text{ \AA} = 0.154 \text{ nm}$$

$$\beta = (0.47 \times 3.14) \div 180 = 0.008$$

$$D = 0.89\lambda \div \beta \cos \theta = 17.377 \text{ nm}$$

The FT-IR spectrum of Co_3O_4 nanoparticles illustrated at Fig. 2 and it showed significant absorption peaks at 567, 661 cm^{-1} . The absorption band at 567 cm^{-1} was assigned to Co-O stretching vibration mode and the peak at 661 cm^{-1} was assigned to the bridging vibration of O-Co-O bond. The weak band near 1600 cm^{-1} is assigned to

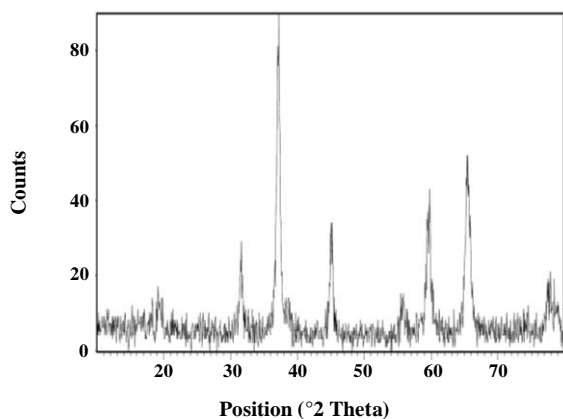


Fig. 1: XRD pattern of the Co_3O_4 nanoparticles calcined at 250 °C.

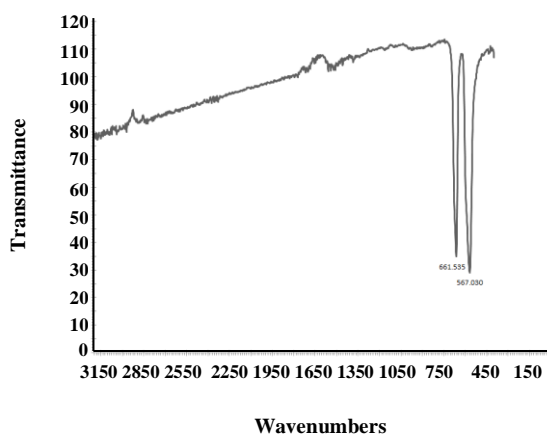


Fig. 2: FT-IR spectrum of Co_3O_4 nanoparticles.

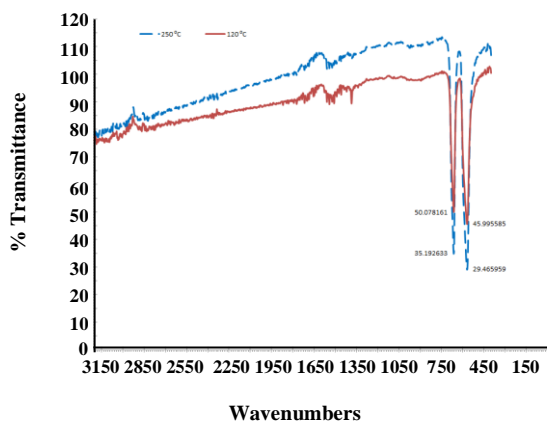


Fig. 3: The FTIR spectrum at 120 and 250 °C.

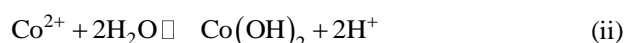
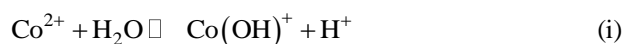
H-O-H bending vibration mode were presented is due to the adsorption of moisture which captures by cobalt oxide when FT-IR sample disks were prepared in an open air atmosphere. Fig. 3 shows the spectrum at two different temperatures. When we heated the sample the impurity material like organic pollutants were eliminated and the bands became purer.

The SEM micrograph of the Co_3O_4 calcined at 250 °C is shown in Fig. 4(a, b). It can be seen that the particles adopt irregular morphology with different sized particle. In addition, Co_3O_4 nanoparticles show rod shape with a smooth surface. The particle's size determined to be between 30 to 46 nanometer.

Fig. 5 (a, b) show the TEM images of the Co_3O_4 nanoparticles. The microstructural characterization studies were conducted to determine the size of nanoparticles and examine the homogeneity and size distribution. It can be seen from Fig. 5 (a) and (b) that there is a uniform distribution of particle size which is in agreement with the XRD result.

Study the Removal of Cd(II) by cobalt oxide nanoparticles

In an aqueous solution of cobalt cation, depending on the pH of the solution, metal ions can present as stable ions or hydrolyses to form a series of mononuclear and polynuclear hydroxyl, for the cobalt hydrolysis is [17]:



Therefore, from reactions (i) and (ii) the adsorption of cadmium ions onto the surface of cobalt oxide is likely to be an electrostatic attraction between the negatively charged surface of the cobalt oxide and the positive cadmium ions.

Effect of pH

Hydrogen ion concentration in the adsorption process is considered as one of the most important parameters that influence the adsorption behavior of metal ions in aqueous solution. The pH of the solution affects the solubility of the metal ions in the solution replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the removal reaction [18]. The calculation from the solubility products equilibrium constant for Cadmium hydroxide

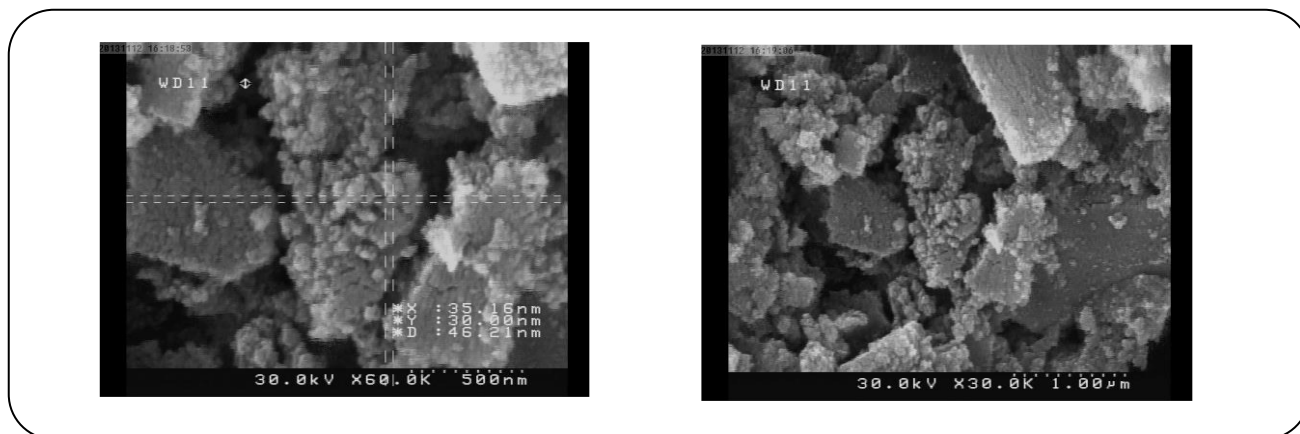


Fig. 4: The SEM micrograph of the Co_3O_4 calcined at 250 °C.

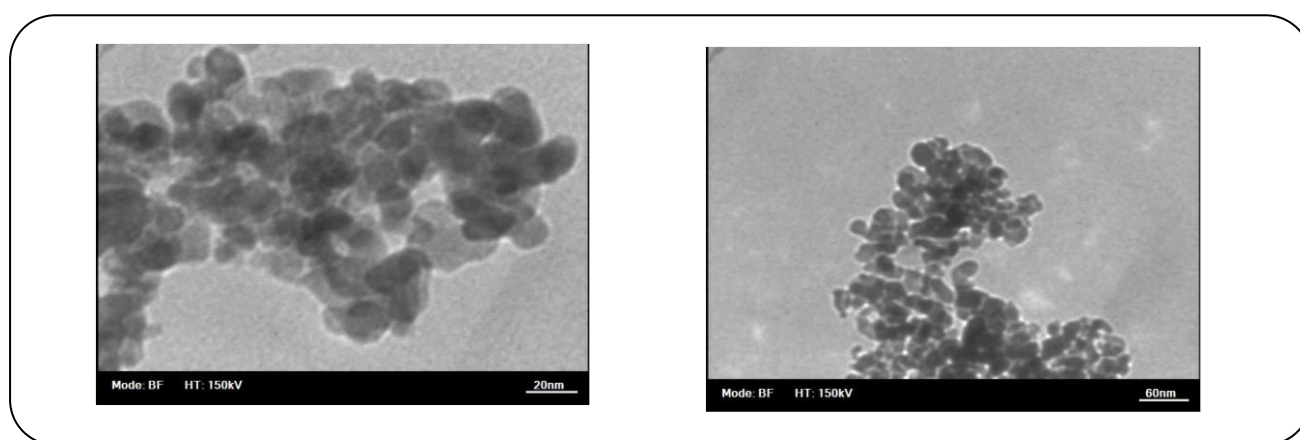


Fig. 5: The SEM micrograph of the Co_3O_4 calcined at 250 °C.

($K_{sp} = 7.20 \times 10^{-15}$) demonstrated that the best pH range of 3-8 for Cadmium(II) removal [19]. In the set of experiments, different samples containing 10, 20 and 30 mg/L of cadmium ion at different initial pH values changing from 3.0 to 8.0 were performed to find the optimum pH for the adsorption of metal ions onto cobalt oxide Nano-adsorbent. The solution of NaOH 0.1 M and HCl 0.1 M were used to adjust the right pH for solutions, and then the prepared solutions were added to 5mg of the adsorbent for 10 minutes in incubator with the speed of 150 revolutions per minute at 25 °C. After centrifuge, the overhead solution was used to read the solution adsorbate of Cd(II) by Atomic Absorbance Spectrometer (AAS). Fig. 6 shows the effect of the solution initial pH on the cadmium ions removal.

Clearly, increasing the pH from 3 to 8.0 increases the ion uptake. The highest adsorption occurs approximately at pH=8.0. Hence, increasing the pH increases the surface deprotonation which, in turn, results in the increase

of the negatively charged sites. This enhances attractive forces between the sorbent surface and the metal ions, and thus results in an increase in the adsorption. In the lower pH region, on the other hand, the positively surface charged sites dominate; this enhances the repulsion forces existing between the sorbent surface and the metal ions and therefore decreases the adsorption.

Buffer Volume Effect

After finding the optimum pH we used borate as an appropriate buffer in this range of pH. The volume of the buffer as another paradigm was investigated. The cadmium solution with the concentration of 10mg/L was prepared with different volume of buffer, then was add to 5mg of adsorbent for 10 minutes in incubator with the speed of 150 RPM at 25 °C. Fig. 7 shows the effect of the buffer volume on the cadmium ions removal. Finally, 1 mL of the buffer was selected as the optimum volume.

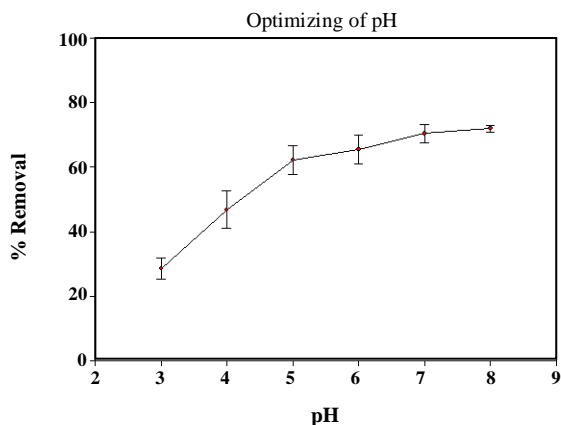


Fig. 6: Effect of pH on cadmium ion adsorption onto cobalt oxide Nano-adsorbents.

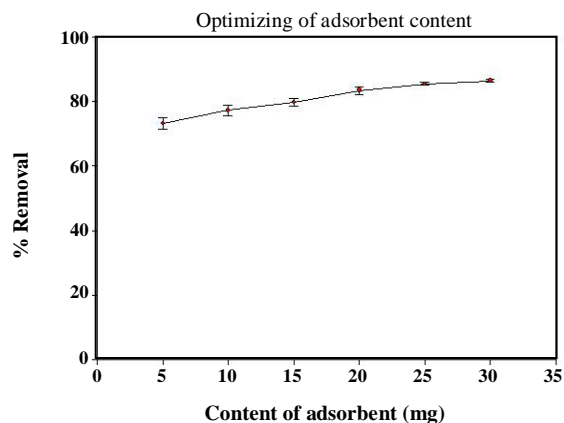


Fig. 8: The effect of adsorbent amount on the cadmium ions removal.

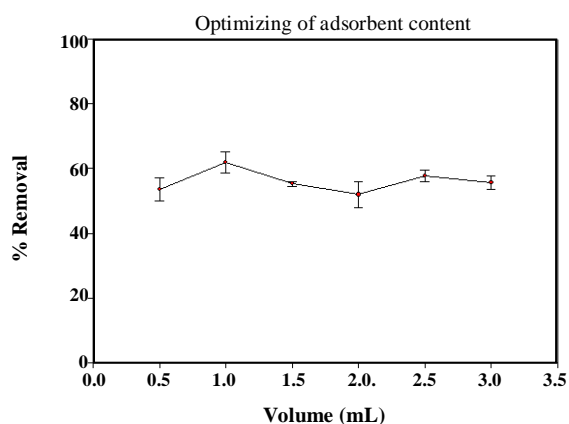


Fig. 7: Effect of the buffer volume on the cadmium ions removal.

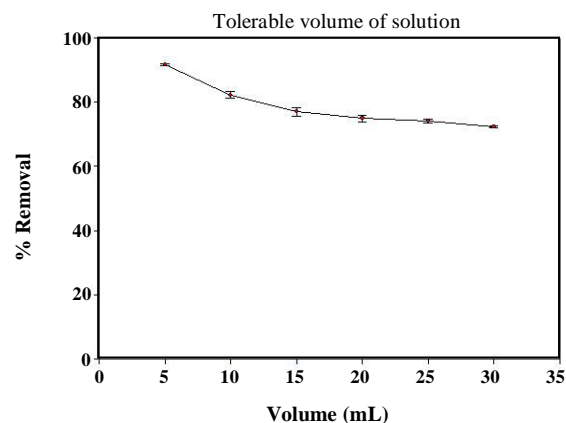


Fig. 9: Bearable Volume for Solution.

The effect of the amount of adsorbent

10 mL cadmium solution with the concentration of 10mg/L and 1mL of borate buffer were prepared. Then we added this amount of solution to various amount of adsorbent from 5 to 30 mg for 10 minutes in the incubator with the speed of 150 RPM at 25 °. After centrifuge, the concentration of Cd(II) was read by AAS. Fig. 8 shows the effect of adsorbent amount on the cadmium ions removal. Finally, 25 mg of the adsorbent has been selected as the optimum amount.

Bearable Volume for Solution

For investigating the bearable volume for solution the 5 to 30 mL of cadmium solution with the concentration of 10mg/L and the 1 mL buffer were prepared. Then the solutions were added to 25 mg of the adsorbent for 10 min in incubator with the speed of 150 RPM at 25 °C. After

centrifuge, the solution adsorbate was read by AAS. Fig. 9 shows the experiment result. The highest removal percentage is attributed to 5mL of the solution.

Contact time Effect

10 mL cadmium solution with the concentration of 10mg/L and 1mL of borate buffer was added to 25 mg of the adsorbent for different contact times from 1 to 60 min in incubator with the speed of 150 RPM at 25 °C. After centrifuge, the solution adsorbate was read by AAS. Fig. 10 shows the contact time effect on cadmium removal. According to Fig. 11, the contact time of 30 min is selected as optimum the contact time.

Temperature Effect

In this study, the effect of temperature on cobalt ion adsorption was performed in the temperature range

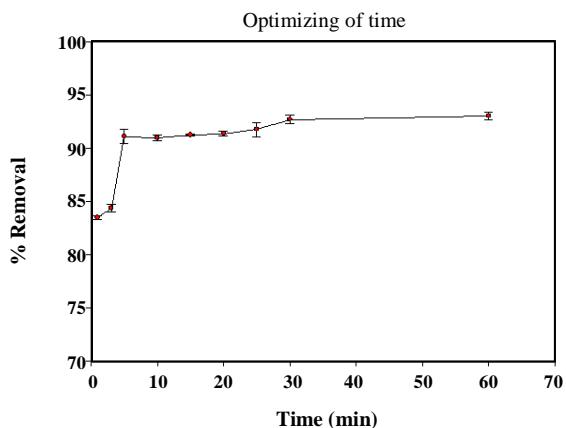


Fig. 10: Time effect on cadmium removal.

of 5–40 °C at pH=8, the solution of 10 mL cadmium solution with 1mL of borate buffer were added to 25 mg of the adsorbent. Then the content of the solution was put in incubator with the speed of 150 RPM in different temperatures. After centrifuge, the solution adsorbate was read by AAS. Fig. 11 shows the temperature effect on cadmium removal.

Process optimization with Taguchi designed experiment

Taguchi method is a statistical method invented by Taguchi and Konishi. At first, it was used for improving the quality of goods manufactured (manufacturing process development), later its application was expanded to many other fields in other fields. Taguchi Method identifies the suitable control factors to receive the optimum results of the process. Here, we try to show the application of Taguchi’s Method to optimize the process.

L₂₅ arrays at the same time were used to study Taguchi designed experiment. Minitab 16 software had been used to do ANOVA variance analysis. According to Fig. 12 the following results have been selected as the optimum for pH, adsorbent content, temperature and contact time respectively: 8, 25 mg, 15 °C and 20 minutes.

Adsorption Isotherms

Adsorption isotherms were conducted for the cobalt oxide nanoadsorbents by varying the initial concentration of cadmium ions from 5 to 25 mg/L at 298 K and pH 8. The Langmuir isotherm model is described by Equation (2):

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

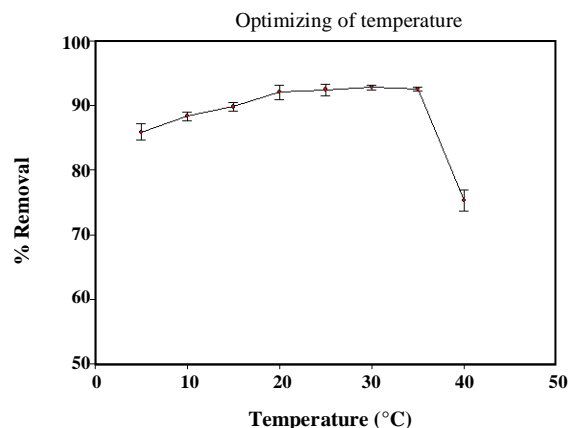


Fig. 11: Temperature effect on cadmium removal.

Where q_e is the number of metal ions adsorbed onto the nanoadsorbents (mol/g), C_e is the equilibrium concentration of metal ions in the supernatant (mol/L), K_L is the equilibrium Langmuir adsorption constant related to the affinity of binding sites (L/mol) and q_{max} is the maximum adsorption capacity for complete monolayer coverage (mol/g). Langmuir constants can be estimated by rearranging Eq. (3) [20] as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{3}$$

By plotting the experimental results as C_e/q_e against C_e , resulted in a straight line which the K_L and q_{max} values were obtained from the slope and the intercept of the best-fit line. Fig. 13 shows the Langmuir plots for cadmium ion at temperature 298 K and solution pH= 8. Clearly, the Langmuir model fits well to the experimental data with correlation coefficients, R^2 , of 0.9736 for Cd(II).

$$q_m = 44.44(\text{mg/g})$$

$$K_L = -0.926(\text{L/mg})$$

The Freundlich [21] model is related to multilayer adsorption mechanism on the heterogeneous surface in which, the adsorption energy of a metal ion is binding to an adsorbent site under influence on whether or not the neighbor sites are already occupied. The linearized form of the Freundlich model is demonstrated by Eq. (4), where, n and K_F are Freundlich constants which are related to adsorption intensity and adsorption capacity, respectively. The values of n and K_F were obtained from the slop and intercept of the $\log q_{eq}$ versus $\log C_e$. Freundlich Isotherm diagram obtained for the selected

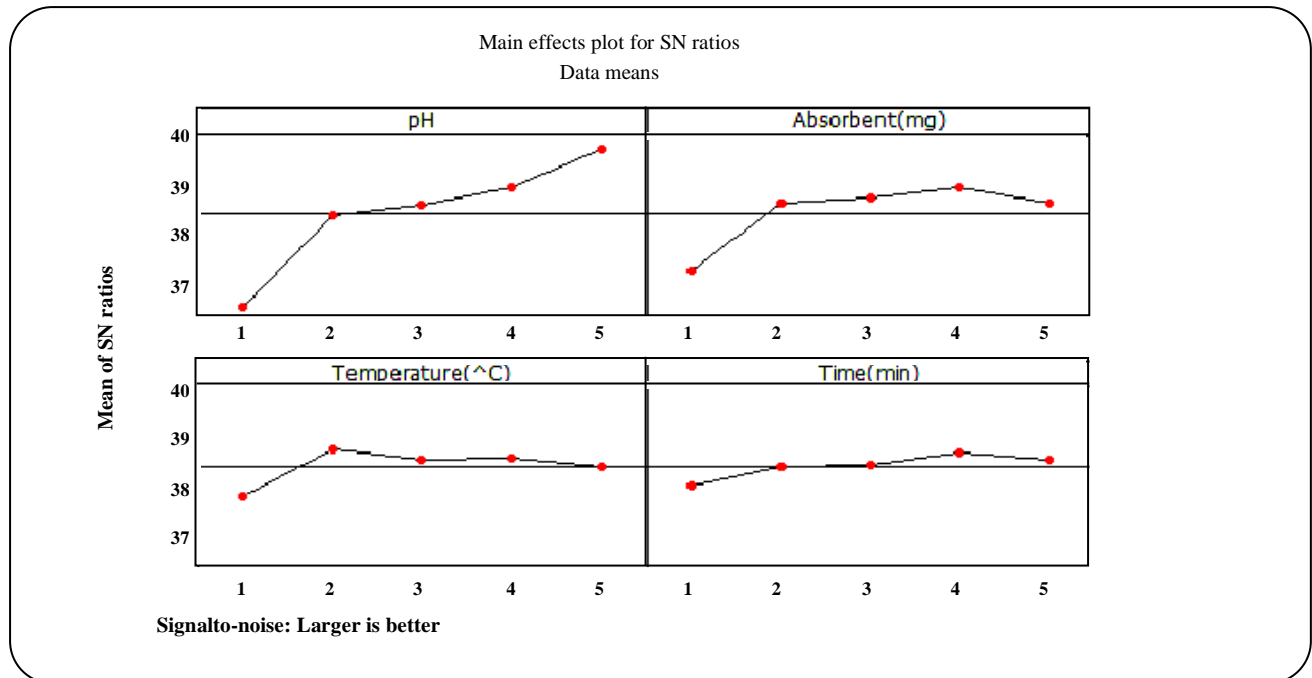


Fig. 12: Process optimization with Taguchi designed experiment.

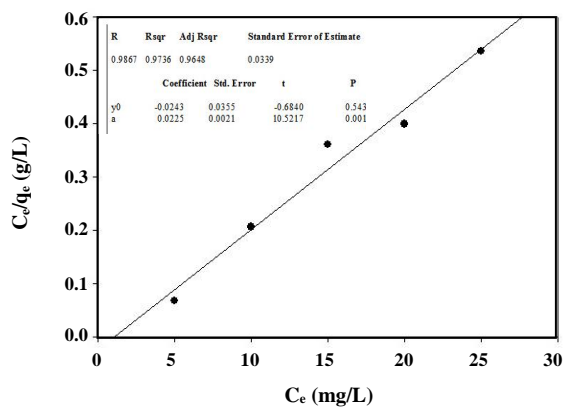


Fig. 13: The Langmuir plots for cadmium ion.

concentrations at 298 K. According to the equation, the K_f and n the Freunlich constants are 2.234 mg/g and 1.48 respectively. Fig. 14 shows the Freundlich plots for cadmium ion.

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The Temkin isotherm model contains a factor that considers the interaction between the adsorbent and adsorbate [22]. The linear form of Temkin isotherm is given by Eq. (5):

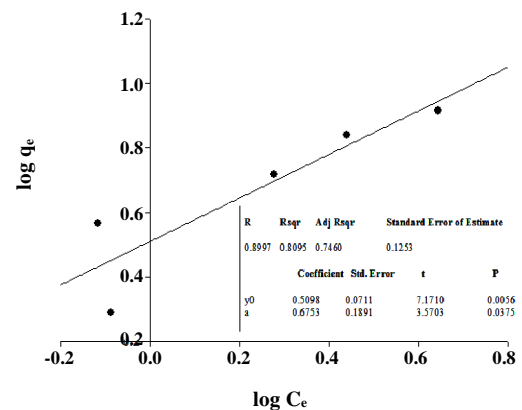


Fig. 14: The Freundlich plots for cadmium ion.

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (5)$$

B_1 and K_T indicate the maximum binding energy kJ/mol that demonstrates the bond between the adsorbent and the adsorbate. B_1 and K_T are Temkin isotherm constants, in which $B_1 = RT/b$ and b (kJ/mol) are related to the adsorption heat. Temkin Isotherm diagram obtained for 5, 10, 15, 25 mg/L of the cadmium ions at 298 K. According the equation the B_1 and K_T are 1.74 kJ/mol and 16.17 L/mg respectively. Fig. 15 shows the Temkin Isotherm for cadmium ion.

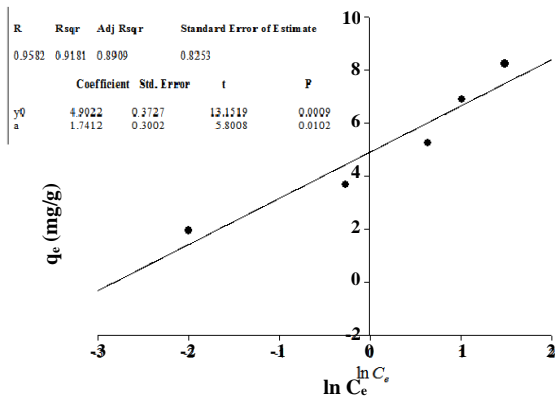


Fig. 15: The Temkin Isotherm for cadmium ion at the optimized condition.

The Dubinin-Radushkevitch (D-R) isotherm Eq. (6) is investigated as well [23]. In this equation q_m is the theoretical isotherm saturation capacity (mg/g) and β and ϵ are D-R constant. D-R Isotherm diagram obtained for 5, 10, 15, 25 mg/L of the cadmium ions concentrations at 298 K. According to the D-R equation (6) the β , q_m and ϵ are 0.043 mol²/kJ², 6.245 mg/g and 3.387 kJ/mol respectively. Fig. 16 shows the D-R Isotherm for cadmium ion.

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (6)$$

The validity of each isotherm model is evaluated with R^2 correlation coefficient, R^2_{adj} adjusted correlation coefficient and standard error of estimate for each model and is listed in Table 1. As is shown in Table 1 the results indicated that the Langmuir model gave a better fit to the experimental data.

Adsorption Kinetics

In order to investigate the adsorption cadmium ions on nanoparticles of cobalt oxide mechanism, the kinetic models have been applied to test the obtained experimental data [24]. In the present study, the well-known kinetic models of first and second-order and Pseudo-first and second order have been applied to the experimental removal data. The first order rate model might have been the first one that used for describing the sorption of liquid-solid systems based on adsorbent capacity.

The linear first order kinetic diagram for 5, 10, 15, 25 mg/L of the cadmium ions at 298 K is presented in

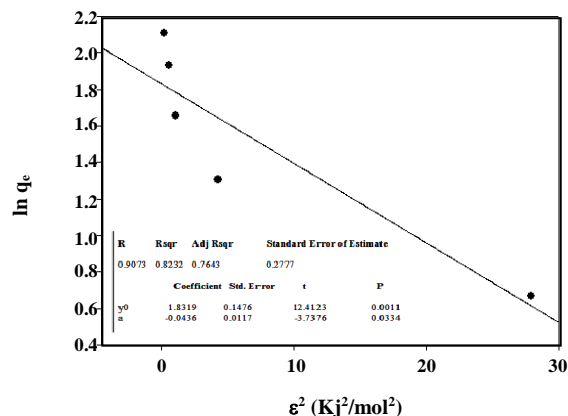


Fig. 16: The D-R Isotherm for cadmium ion at the optimized condition.

Fig. 17. According to first order equation, Eq (7) where C_t and C_0 are the concentration of cadmium ions at the time of t and at start point of the process and k_1 is rate constant, therefore the k_1 of this experiment is 0.004 min⁻¹. Fig. 17 shows the linear graph of the first order adsorption kinetic of cadmium ion over nanoparticles of cobalt oxide.

$$\ln C_t - \ln C_0 = -k_1 t \quad (7)$$

The linear pseudo-First order kinetic diagram for 5, 10, 15, 25 mg/L of the cadmium ions at 298 K is shown in Fig. 18. According to the equation of pseudo first order equation (8), Where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and at the time t and k_1 is the rate constant of Pseudo- first-order, therefore for this experiment, the k_1 is 0.028 min⁻¹. Fig. 18 shows the pseudo-first order adsorption kinetic of cadmium ion by nanoparticle of cobalt oxide.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

The second order kinetic diagram for 5, 10, 15, 25 mg/L of the cadmium ions at 298 K is presented in Fig. 19. According to the equation (9) where C_t and C_0 are the concentration of cadmium ions at time of t and at the start point of the process and k_2 is the rate constant, therefore the k_2 for this experiment is 0.004 mg/g.min. Fig. 19 shows the second order kinetic of adsorption of cadmium ion over nanoparticles of cobalt oxide.

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_0} \quad (9)$$

Table 1: Isotherm models parameters for adsorption of Cd(II) over nanoparticles of cobalt oxide.

| Isotherm Model | R ² | R ² _{adj} | Standard Error of Estimate |
|----------------------|----------------|-------------------------------|----------------------------|
| Langmuir | 0.9736 | 0.9648 | 0.0339 |
| Freundlich | 0.8095 | 0.7460 | 0.1253 |
| Temkin | 0.9181 | 0.8909 | 0.8253 |
| Dubinin-Radushkevith | 0.8232 | 0.7643 | 0.2727 |

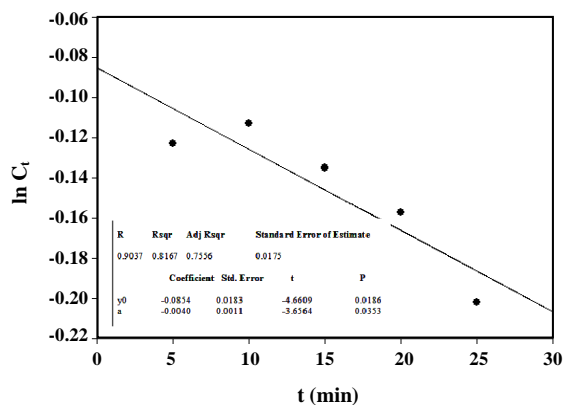
**Fig. 17: First order kinetic model of adsorption of cadmium ions by nanoparticles of cobalt oxide.**

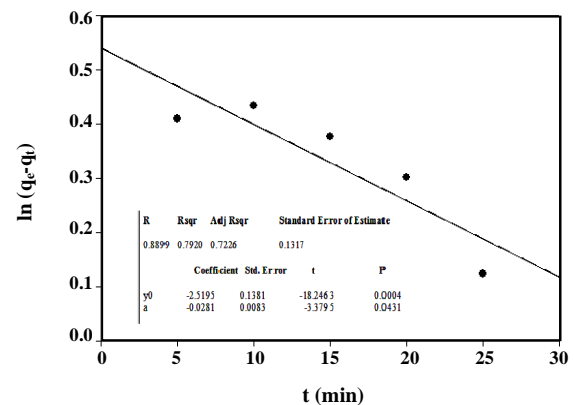
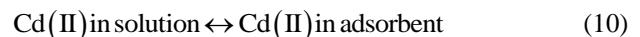
Fig. 20 shows that the linear graph of the pseudo second order kinetic of adsorption of cadmium ions by nanoparticles of cobalt. According to the equation of pseudo second order equation (10), where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and at the time t and k_2 is the rate constant of Pseudo- second order. The linear plot of t/q_t vs. t is shown in Fig. 20, the k_2 and q_e values are calculated from slope and intercept of this plot respectively thus for this experiment the calculations are, $k_2=3.359$ g.min/mg and $q_e= 3.679$ mg/g.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

The Kinetic parameters are calculated and shown in Table 2. The comparison between R^2 , R^2_{adj} and Standard error of estimate values for the four models demonstrates that the adsorption process was better fitted in the Pseudo-second order kinetic model with a higher correlation and lower degree of difference.

Thermodynamics Studies

The mechanism of Cd(II) adsorption is illustrated by the following reversible process, which happens in the heterogeneous surface at the equilibrium state:

**Fig. 18: Pseudo-first order kinetic model adsorption of cadmium ions by nanoparticles of cobalt oxide.**

The thermodynamic equilibrium constant (K_C) for the adsorption process was determined, using Eq. (11):

$$K_C = \frac{C_a}{C_e} \quad (11)$$

Here, C_a and C_e are the Cd(II) concentration on the adsorbent and the solution at equilibrium, respectively. The thermodynamic equilibrium constant is related to Gibbs free energy change using the Van't Hoff equation.

$$\Delta G^0 = -RT \ln K_C \quad (12)$$

Where, ΔG^0 is standard Gibbs free energy change, R , is universal gas constant and $T(K)$, is temperature of the adsorption process. According to the thermodynamic relationship, Gibbs free energy change is dependent on the enthalpy and entropy changes of adsorption at a constant temperature. The Values of thermodynamic parameters, such as changes in standard Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) that describe the adsorption process were calculated using the above Eq. (12). The equilibrium

Table 2: Kinetics models parameters for adsorption of Cd(II) by nanoparticles of cobalt oxide.

| Kinetic Model | R ² | R ² _{adj} | Standard Error of Estimate |
|---------------------|----------------|-------------------------------|----------------------------|
| First Order | 0.8167 | 0.7556 | 0.0175 |
| Pseudo First Order | 0.7920 | 0.7226 | 0.1317 |
| Second Order | 0.8068 | 0.7424 | 0.0210 |
| Pseudo Second Order | 1.0000 | 1.0000 | 0.0119 |

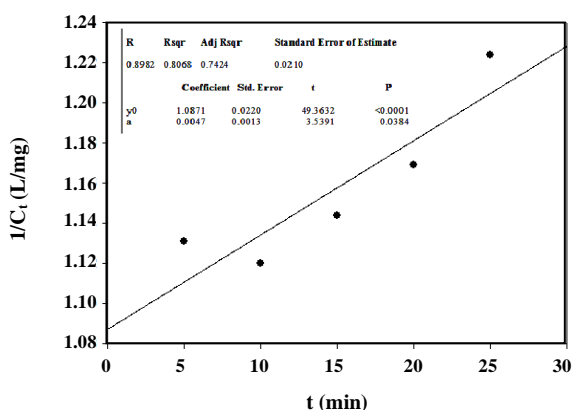


Fig. 19: The graph of liner second order kinetic model of adsorption of cadmium ions by nanoparticles of cobalt oxide.

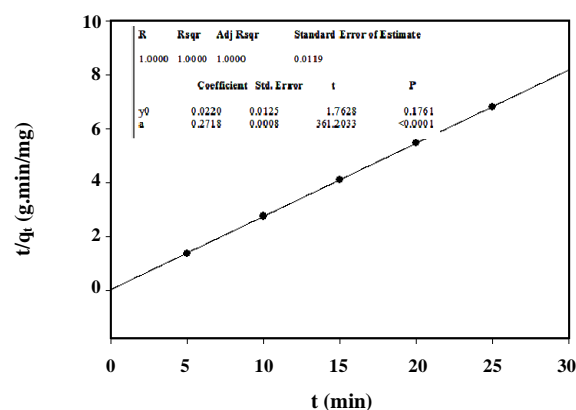


Fig. 20: Pseudo-second order model adsorption kinetics of cadmium.

constant, K , can be approximately estimated by using the following equation (13):

$$K = K_L C_{\text{Solvent}} \quad (13)$$

Where K_L is the equilibrium Langmuir constant (L/mmol) and C_{solvent} is the solvent molar concentration (mM), which is estimated from the density and molecular weight of water at the given temperature [25]. ΔH° and ΔS° were determined from the van't Hoff equation (14) that showed the dependence of equilibrium constant of the adsorption process on the temperature as follows [26]:

$$\ln K = -\Delta H/RT + \Delta S/R \quad (14)$$

$$\Delta H_{\text{ads}}^\circ = 22.381 \text{ (kJ/mol)}$$

The van't Hoff plot is shown in Fig. 21 for Cd ions, The plot of $\ln(K)$ against $1/T$. $\Delta H_{\text{ads}}^\circ$ were calculated from slope and $\Delta S_{\text{ads}}^\circ$ from the intercept of the best fit line. The $\Delta G_{\text{ads}}^\circ$ values calculated from Gibbs's equation. The value found for $\Delta G_{\text{ads}}^\circ$ and $\Delta S_{\text{ads}}^\circ$ at all temperature are presented in Table 3. The values of $\Delta G_{\text{ads}}^\circ$ at all temperature were negative indicating the spontaneous nature and thermodynamically favorable adsorption reaction. The further increase in the negative value of

$\Delta G_{\text{ads}}^\circ$ shows the stronger the driving force of the adsorption process. The positive value for $\Delta H_{\text{ads}}^\circ$ confirms the endothermic nature of the adsorption Cd(II) ions onto nanoparticles of cobalt oxide. Because diffusion is an endothermic process, therefore one expected an increase in the solution temperature, which results in an increase in the adsorption of Cd(II) ions from aqueous solution onto nanoparticles of cobalt oxide surface. The positive values of $\Delta S_{\text{ads}}^\circ$ are attributed to the increase in randomness at the solid-liquid interface that resulted from the extra translational entropy gained by the water molecules previously adsorbed onto nanoparticles of cobalt oxide but displaced by Cd(II) ions.

As Seki and Yurdakoc mention that adsorption reaction with $\Delta G_{\text{ads}}^\circ$ values between -20 and 0 kJ/mol indicates a spontaneous physical adsorption reaction, while that with values between -400 and -80 indicates chemisorption [27]. In this study, the $\Delta G_{\text{ads}}^\circ$ values were between -4 and -6 kJ/mol, which can be deduced that the adsorption mechanism is attributed to physical adsorption enhanced by a chemical effect. This also is supported by the fact that $\Delta H_{\text{ads}}^\circ < 40$ kJ/mol indicating a physical adsorption process.

Table 3: Estimated of ΔG° and ΔS° of the adsorption of Cd ions onto cobalt oxide nanoparticles at different temperatures.

| Temperature (K) | 278 | 283 | 288 | 293 | 298 | 303 |
|---|--------|--------|--------|--------|--------|--------|
| $\ln K_c$ | 1.810 | 2.029 | 2.177 | 2.456 | 2.509 | 2.565 |
| $\Delta G^\circ_{\text{ads}}(\text{kJ}\cdot\text{mol}^{-1})$ | -4.183 | -4.774 | -5.213 | -5.983 | -6.216 | -6.461 |
| $\Delta S^\circ_{\text{ads}}(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$ | 95.5 | 95.9 | 95.8 | 96.8 | 95.9 | 95.1 |

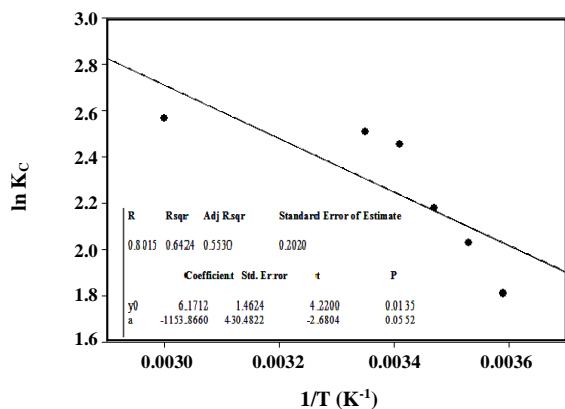


Fig. 21: Van't Hoff plots for the endothermic adsorption of Cd ions onto nanoparticles of cobalt oxide.

CONCLUSIONS

The adsorbent, cobalt oxide was synthesized by sol-gel method, which was used for removal of Cd(II) ions from aqueous solution. The characterization of the adsorbent was done by XRD, SEM, TEM, and FT-IR. The results show the nanoparticles of cobalt oxide are form in the powder. In the study of removal of cadmium ions in aqueous solution by cobalt oxide the number of factors was optimized. The Factors that have been optimized in this study were: pH=8, buffer volume= 1 mL, adsorbent amount=25 mg, Bearable Volume for Solution=5 mL, contact time=30 minutes at 25 °C for temperature. To find the adsorption isotherm model of the process, four isotherm models were investigated, and the adsorption isotherms were determined and appropriately described the experimental data by Langmuir model. The thermodynamic studies confirmed that the adsorption process of Cd(II) onto nanoparticle of cobalt oxide was spontaneous, endothermic and physical in nature. The evaluation of the thermodynamic parameters, such as ΔG° , ΔH° and ΔS° of the adsorption process were calculated.

Received : Sep. 7, 2017 ; Accepted : Jan. 31, 2018

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