

Adsorption and Optimization Removal of Co(tsPc)⁻⁴ from aqueous solution using Nanoalumina

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Abstract

In the present study, adsorption of Co(tsPc)⁻⁴ using γ -Alumina was investigated. γ -Alumina was prepared by gel combustion method. The XRD pattern revealed that the synthesized γ -Alumina is amorphous and SEM image showed its nanosize scale while BET surface area about 501 m²/g and pore size of 7 nm implies highly porous surface which is a characteristic property of a high-quality adsorbent. In the second step of this study, the effects of adsorbent dosage, initial Co(tsPc)⁻⁴ concentration and contact time were investigated. Upon the obtained UV-Vis spectra, λ_{max} of 664 nm was used to determine the concentration of Co(tsPc)⁻⁴ after adsorption. From the Langmuir isotherm the maximum adsorption capacity of γ -Alumina toward Co(tsPc)⁻⁴ was determined ($Q_m=333.33$ mg/g). Although Co(tsPc)⁻⁴ adsorption occurred in the first 40 min of contact time, at least 90 min time was needed to attain equilibrium. The kinetics of adsorption can be described by second order rate equation. After that, statistically based experimental design, i.e. as Box–Behnken design (BBD), was used to study the effect of independent variables on the adsorption. Regeneration studies of the adsorbent were carried out and it was found that the adsorbent can be effectively regenerated up to 3 times with no significant deactivation. The obtained results suggest γ -Alumina is high quality adsorbent for the removal of Co(tsPc)⁻⁴ from aqueous waste streams in different industries such as painting and oil & gas in MEROX unit.

Keywords: adsorption; γ -Alumina; Aqueous solutions; Box–Behnken design; Isotherm

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1.Introduction

Sulfur-containing compounds, such as mercaptans, alkali sulfites, and alkali thiosulfates are by-products of industrial processes and pollutants of waste and natural waters [1]. The complete oxidation of sulfur-containing compounds, before discharging them into waterways, has been suggested as a possible solution of the environmental pollution problem. Phthalocyanine complexes are effective catalysts and photocatalysts for thiol and hydrosulfide oxidation by dioxygen [2]. The activation of dioxygen and the possibility of its participation in a catalytic or photocatalytic process is dependent on the electronic structure of the phthalocyanine complexes and the central metal atom [3].

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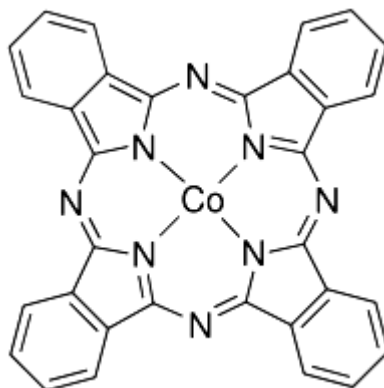


Figure 1. Chemical structure of $\text{Co}(\text{tspc})^{-2}$

Phthalocyanine complexes containing metal ions with unfilled d orbitals, like Co^{+2} , can reversibly coordinate and activate dioxygen in the dark which is the basis of the redox mechanism of catalytic oxidation of sulfur-containing compound Figure1 (1). These catalysts have found wide application in the catalytic oxidation of mercaptans in oil fractions. The oxidation of thiols by cobalt phthalocyanine complexes - CoPc , is not complete, the end products being disulfides (2).

In the present work, γ -Alumina was prepared by sol-gel method and the synthesized nanoparticle was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The effects of adsorbent dosage, initial $\text{Co}(\text{tspc})^{-4}$ concentration and contact time were studied. The adsorption was fit to different adsorption isotherms and also to kinetics of the adsorption was studied. Parameters affecting the removal of $\text{Co}(\text{tspc})^{-4}$ from the aqueous solution was investigated and validated by using three factorial Box- Behnken design (BBD).

2. Materials and methods

2.1. Synthesis of $\gamma\text{-Al}_2\text{O}_3$

Synthesis of $\gamma\text{-Al}_2\text{O}_3$ was carried out via method reported by Bao et.al. with minor modification(1). Briefly, 1 gr of NaOH was added to distilled water add the 10 mL of AlCl_3 solution (0.6 M) was added dropwise to the caustic solution while stirring. After that, 20 mL of ethanolic solution of CTAB (0.05 M) and 0.2 g of PEG 5000 (MW) was added to the above mixture. Prior to autoclave for 12 h at 160 °C, the mixture was stirred 24 hours at ambient condition. Then, the obtained white powder was filtered and washed thoroughly with distilled water until neutralization of rinsed water and calcined at 600 °C for 4 h.

2.2. Characterization methods

To understand the morphology of the γ -alumina, a scanning electron microscope (SEM) was used. The structure of alumina was studied with the help of an Xray diffractometer. XRD analysis was done using $\text{Cu-K}\alpha$ as a source and Ni as a filter media, and K radiation maintained at 1.542 Å. Goniometer speed was kept at 2° min^{-1} . The range of scanning angle (2θ) was kept at 10–100°. The intensity peaks indicate the values of 2θ , where Bragg's law is applicable. The identification of compounds was done using the ICDD library. Textural characteristic of the alumina was determined by nitrogen adsorption at 77.15K. The Brunauer–Emmett–Teller (BET) surface area(3) and monolayer pore volume of the alumina was determined using the software available with the instrument.

3. Results and discussion

3.1. Characterization of γ -Alumina

3.1.1 SEM analysis:

Figure 2 shows the SEM image of the synthesized γ -Alumina. to study the surface morphology of the γ -Alumina nano-particle.

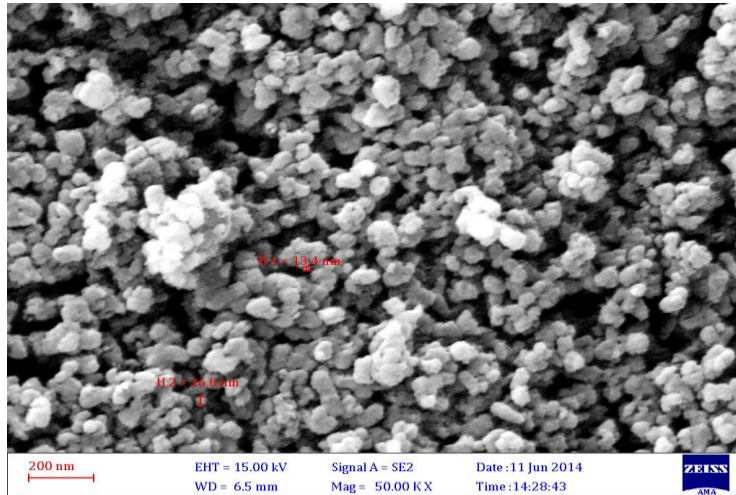


Figure 2. SEM images of γ -Alumina.

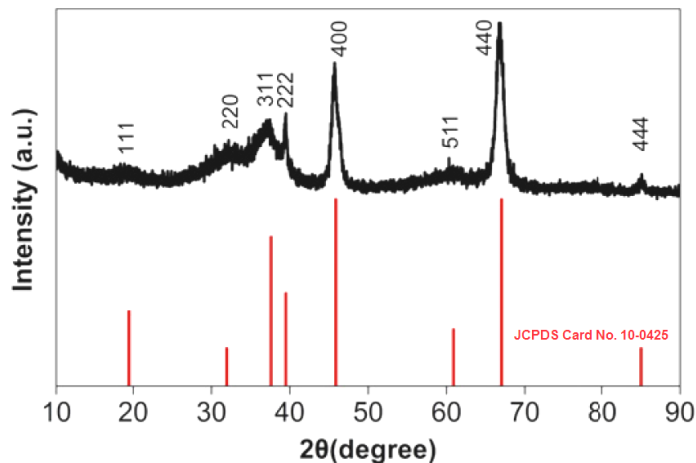


Figure 3. Typical XRD pattern of γ -Alumina

3.1.2 XRD analysis:

The structure of synthesized particles is investigated by X-ray diffraction. Figure 3 shows the XRD patterns of γ -Alumina particles synthesized by sol-gel method(1). The XRD pattern depicts that the synthesized γ -Alumina is amorphous in nature and the broad peaks indicate that the synthesized γ -Alumina particles are of nano size.

3.1.3 Determination of surface area and pore size:

The surface area of the calcinated γ -Alumina was determined by nitrogen physisorption using Micrometrics Flow sorb 2300. Before each measurement the calcinated sample was degassed at 400°C for 2 h. To measure the nitrogen adsorption/desorption isotherms. BJH model was used to determine the pore-size distribution. The surface area of the γ -Alumina after calcination was found to be 370 m²/g. The mean pore diameter was found to be 7 nm.

3.2 Adsorption experiments

Adsorption behaviour was studied by a batch method, which parameters that influence the adsorption process such as contact time, initial concentration and adsorbent dosage was investigated. aqueous solutions of Co(tsPc)⁻⁴ with concentration ranging from 100 to 700 ppm were prepared by dissolving Co(tsPc)⁻⁴ in double distilled water.

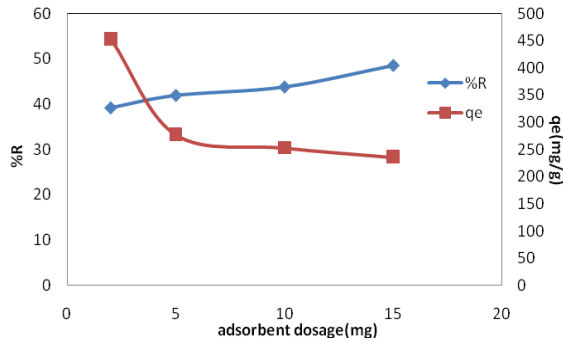


Figure 4. Effect of adsorbent dosage on the adsorption of Co(tsPc)⁻⁴

In each adsorption experiment, 10 mg adsorbent was added in 10 mL Co(tsPc)⁻⁴ solutions. After equilibrium, the concentration of the adsorbate in the residual solution was analyzed by a UV-spectrophotometer at λ max of 664 nm. The amount of Co(tsPc)⁻⁴ adsorbed per unit mass of γ-Alumina the q_e (mg g⁻¹) was calculated by the following equation (1) :

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

Where q_e is the adsorption capacity (mg g⁻¹) of the adsorbent at equilibrium; C₀ and C_e are the initial and equilibrium concentrations of solute (mg L⁻¹), respectively; V is the volume of the aqueous solution (L) and W is the mass (g) of adsorbent used in the experiments.

The adsorptive removal efficiency (R) was determined according to the following equation:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

3.3 Effect of adsorbent dosage

To determine the effect of dosage of γ-Alumina on adsorption of Co(tsPc)⁻⁴ a batch study was set up. The initial dosage amount of adsorbent was varied from 2 to 15 mg. γ-Alumina was added to 10ml of 500ppm Co(tsPc)⁻⁴ solution in flasks. The mixture was subjected to adsorption in shaker for 90 min. After adsorption, the mixture was filtered, centrifuged and analyzed for Co(tsPc)⁻⁴ concentration. It can be seen from figure 4 that the percentage removal increases with increase in the adsorbent dosage. The increasing of removal percentage with increases sorbent dosage is because of the availability of more adsorption and exchange sites for Co(tsPc)⁻⁴ and then by overlapping of active sites, equilibrium was established between the sorbent and Co(tsPc)⁻⁴(5) . It can also be seen that the plot of amount removed per unit mass of sorbent, q (mg/g), decreased as sorbents dosage was increased. The reason could be that the available active sites remain unsaturated during the removal by increasing the sorbent concentration. Therefore 10 mg was considered sufficient for quantitative removal of Co(tsPc)⁻⁴ by γ-Alumina from aqueous solutions (6).

3.4 Effect of contact time

The rate and quantity of adsorbate adsorbed by the adsorbent is limited by the size of adsorbate molecules, concentration of adsorbate and its affinity towards the adsorbent, diffusion coefficient of the adsorbate in the bulk and solid phase, the pore size distribution of the adsorbent, and degree of mixing. 10 mg γ-Alumina was added to 10ml of 500ppm Co(tsPc)⁻⁴ solution in flasks. As seen in Figure 5, the adsorption rate is fast at initial times and then it gradually decreases until equilibrium has reached. A large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases (7). Besides, the Co(tsPc)⁻⁴ is adsorbed into the pores that get almost saturated with Co(tsPc)⁻⁴ during the initial stage of adsorption. Thereafter, the Co(tsPc)⁻⁴ have to traverse farther and deeper into pores encountering much larger resistance. This results in the slowing down of the adsorption during the later period of adsorption.

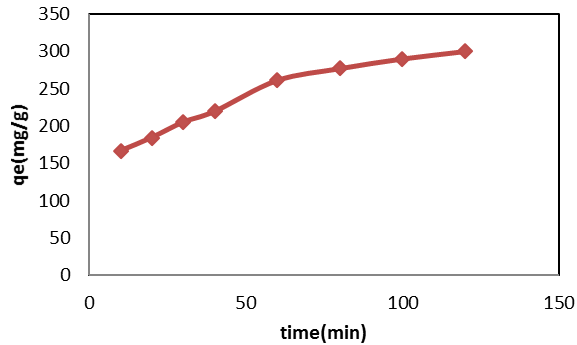


Figure 5. Effect of contact time on the adsorption of Co(tsPc)⁻⁴

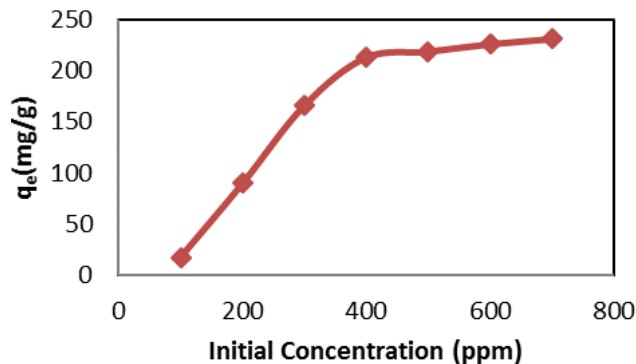


Figure 6. Effect of initial concentration on the adsorption of Co(tsPc)⁻⁴

3.5 Effect of initial Co(tsPc)⁻⁴ concentration

Batch adsorption studies were carried out for various Co(tsPc)⁻⁴ concentrations ranging from 100 to 700 ppm using γ -Alumina to study the effect of initial Co(tsPc)⁻⁴ concentration on adsorption. 10ml of 100–700ppm Co(tsPc)⁻⁴ solution was taken in 7 different flasks. 10mg of γ -Alumina was added to each flask. The adsorption mixture was subjected to adsorption in shaker for 60 min at room temperature ($25\pm 3^\circ\text{C}$). The adsorption mixture was then filtered, centrifuged. The amount of Co(tsPc)⁻⁴ adsorbed per unit mass of alumina increased with an increase in C_0 (Figure 6). The amount adsorbed increased with an increase in the adsorbate concentration due to the decrease in the resistance for the uptake of Co(tsPc)⁻⁴ from the solution(8).

3.6 Equilibrium and isotherm study

Adsorption isotherms help in optimizing the use of γ -Alumina as an adsorbent. Empirical equations play a major role in data interpretation and predictions. In the present work, batch adsorption tests were carried out to validate Langmuir(9), Freundlich(10) and temkin(11) adsorption isotherms. The Langmuir isotherm is a useful isotherm model for describing both physical and chemical sorption. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. Langmuir isotherm is given by Eq(12).

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (\text{B})$$

where C_e (mgL^{-1}) is the equilibrium concentration, q_e (mgg^{-1}) the amount of adsorbate adsorbed per unit mass of adsorbent, q_m (mg g^{-1}) is the Langmuir constant representing maximum monolayer capacity and b is the Langmuir constant related to the energy of adsorption. The Langmuir constants b and q_m were calculated from this isotherm and their values are listed in table 1.

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy. Freundlich model is given in Eq(13).

$$\log q_e = \log K_F + 1/n \log C_e \quad (\text{C})$$

Table1. Parameters calculated from fitting the results of adsorption isotherm of Co(tsPc)⁻⁴ onto γ-Alumina to different models.

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
q _m (mg g ⁻¹)	b (L mg ⁻¹)	R ²	K _F (mg g ⁻¹)	N (L mg ⁻¹)	R ²	K _T	B	R ²
333.33	0.048	0.997	11.92	5.235	0.853	2.52	40.41	0.858

where K_f is the Freundlich constant (mg g⁻¹ (mg L⁻¹)ⁿ) and 1/n is the heterogeneity factor. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The plot of log q_e versus log C_e, gives straight lines with slope 1/n.

The temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The Temkin isotherm is given as (14):

$$q_e = BLn k_t + BLn c_e \tag{5}$$

K_t is the equilibrium binding constant (Lmg⁻¹) corresponding to the maximum binding energy and constant B is related to the heat of adsorption. From Table 1, the Langmuir isotherm model yielded the best fit with the highest R² value (0.99) compared to the other two models.

3.7 Kinetics study

Adsorption kinetics is one of the major characteristics which represent the efficiency of the adsorbent. It helps in determining the potential applications of the adsorbent(15, 16) . during the first 60 min of contact time, there is a significant increase in the Co(tsPc)⁻⁴removal by γ-Alumina. As the void sites fill up with time, gradually the rate of removal decreased after 60 min. It can be inferred that, the removal of Co(tsPc)⁻⁴takes place in two distinct steps: a relatively fast step followed by a slower one. The necessary time to reach equilibrium is approximately 90 min. The kinetics of Co(tsPc)⁻⁴removal by γ-Alumina was studied, using the pseudo first order and the pseudo second order models.

The pseudo- first-order equation can be used to determine the rate constant for the adsorption process and describe the initial stage of the adsorption process as follows(17):

$$\frac{1}{q_t} = \frac{k_1}{q_e} \left(\frac{1}{t}\right) + \frac{1}{q_e} \tag{6}$$

where q_e and q_t are the amounts of adsorbed Co(tsPc)⁻⁴ at equilibrium and any time t (mg g⁻¹), respectively, k₁ is the equilibrium rate constant of the first-order sorption (min⁻¹).

The pseudo-second-order rate equation of can be represented in the following form(18):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where K₂ (g mg⁻¹ min⁻¹)is the rate constant of the second-order equation, q_t (mg g⁻¹) and q_e (mg g⁻¹) Co(tsPc)⁻⁴ adsorbed at time t (min) and at equilibrium, respectively.

Table 2. Pseudo-first-order and Pseudo-second-order kinetic model for adsorption of Co(tsPc)⁻⁴ on γ- Alumina

pseudo-second-order			pseudo-second-order		
q _e (mg g ⁻¹)	K ₁ (L min ⁻¹)	R ²	q _e (mg g ⁻¹)	K ₂ (g mg ⁻¹ min ⁻¹)	R ²
250	5	0.934	333.33	0.00036	0.996

Table 3. List of variables and their levels considered for BBD

Factor	+1	0	-1
Concentration(mg/l)	600	350	100
(min) Contact time	100	10	55
(mg) Adsorbent dosage	15	8.5	2

Pseudo-second-order kinetics is based on the adsorption capacity, which usually gives a good description of the whole adsorption process. The rate constants and correlation coefficients of the two kinetic models can be obtained from the plot of experimental data (Table 2). pseudo-second-order kinetic with the higher correlation coefficient (R^2) suggests that Co(tsPc)⁻⁴ adsorption on to γ -Alumina predominantly follows the pseudo-second-order kinetic model.

3.8. Box-Behnken design (BBD)

Statistical based experimental designs are more efficient in adsorption studies as compared to traditional approach. The effects of all the three variables (contact time, initial concentration of Co(tsPc)⁻⁴ and adsorbent dosage) on adsorption are studied using Box-Behnken design (BBD). Box-Behnken designs are a class of rotatable or nearly rotatable second order designs based on three level factorial designs_ENREF_21(19, 20). In order to investigate and validate the parameters affecting the removal of Co(tsPc)⁻⁴ from the aqueous solution. In the present work three factorial BBD experimental design was used. Table 3 gives the detailed list of levels for BBD. Based on the BBM factor method, the following analysis was made and the percentage removal was calculated experimentally. Table 3 gives the BBD experimental design plan of the optimization design with experimental and predicted values of adsorption. In the Box-Behnken design, 17-experimental observations were undertaken at random orders for the optimization percentage remove Co(tsPc)⁻⁴ from the aqueous solution.

To investigate the effects of main factors and their interactions analysis of variances (ANOVA) was used. The results of the second order response surface model fitting in the form ANOVA are given in table 4. The "Pred R-Squared" of 0.9701 is in reasonable agreement with the "Adj R-Squared" of 0.9920. "Adeq Precision" measures the signal to noise ratio. The Model F-value of 19.21 implies that the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. The large value of F indicates that the most of the variation in the response can be explained by the regression equation.

Table 4. ANOVA of the model for adsorption of Co(tsPc)⁻⁴ on γ -Alumina. from Box-Behnken.

Source	Sum of squares	Df	Mean Square	F Value	P-value	Prob>F
Mode	4587.02	9	509.67	19.21	0.0004	Significant
A-C	511.84	1	511.84	19.30	0.0032	Significant
B-t	1361.38	1	1361.38	51.32	0.0002	Significant
C-m	1520.49	1	1520.49	57.32	0.0001	Significant
AB	10.56	1	10.56	0.4	0.5481	Not-Significant
AC	111.83	1	111.83	4.22	0.0791	Significant
BC	372.1	1	372.1	14.03	0.0072	Significant
A ²	446.02	1	446.02	16.81	0.0046	Significant
B ²	10.45	1	10.45	0.39	0.5502	Not-Significant
C ²	216.59	1	216.59	8.17	0.0244	Significant
Pure Error	139.86	4	34.96	-	-	
Cor Total	4772.69	16		-	-	

Values of “Prob > F” less than 0.0500 indicate that the model terms are significant. In this case A, B, C, AC, BC, A², C² are significant model terms. A quadratic model with statistical significance from a combination of estimates for the variables and the ANOVA results can be produced. The quadratic model was used to explain the mathematical relationship between the independent variables and dependent responses which is represented by terms of coded factors Eq:

Figure 7.a depicts the effect of contact time and adsorbent dosage on the adsorption of Co(tsPc)⁻⁴ onto the surface of γ-Alumina. With the increase in loading of γ-Alumina and contact time of the solution the percentage remove increases. The increase in the adsorbent dosage provides more surface area for adsorption.

Figure 7.b depicts the effect of initial concentration and adsorbent dosage on the percentage remove. With the increase in the adsorbent dosage the number of binding sites increase, but with the increase in the initial concentration of Co(tsPc)⁻⁴, the availability of free binding sites decreases. Hence with the increase in the adsorbent dosage and initial concentration of the solution, the percentage remove in first increases and them decreases.

$$R = -5.28232 + 0.063565X_c + 0.53516X_t + 5.68158X_m - 1.44444 \times 10^{-4} X_c \cdot X_t + 3.25385 \times 10^{-3} X_c \cdot X_m - 0.032974 X_t \cdot X_m - 1.64676 \times 10^{-4} X_c^2 + 7.77901 \times 10^{-4} X_t^2 - 0.16976 X_m^2 \quad (8)$$

Table 5. Box–Behnken method experimental plan for adsorption of Co(tsPc)⁻⁴ on γ-Alumina.

Blank	Concentration (mg/l)	Time(min)	Adsorbent dosage (mg)	%R
1	350	10	2	12.85
2	100	100	8.5	68
3	100	55	15	56
4	350	100	2	62.57
5	600	10	8.5	30
6	100	55	2	37
7	100	10	8.5	43
8	350	100	15	68.85
9	350	55	8.5	54.2
10	600	100	8.5	48.5
11	600	55	15	50.83
12	350	10	15	57.71
13	350	55	8.5	52.42
14	600	55	2	10.68
15	350	55	8.5	50.28
16	350	55	8.5	52.71
17	350	55	8.5	53.85

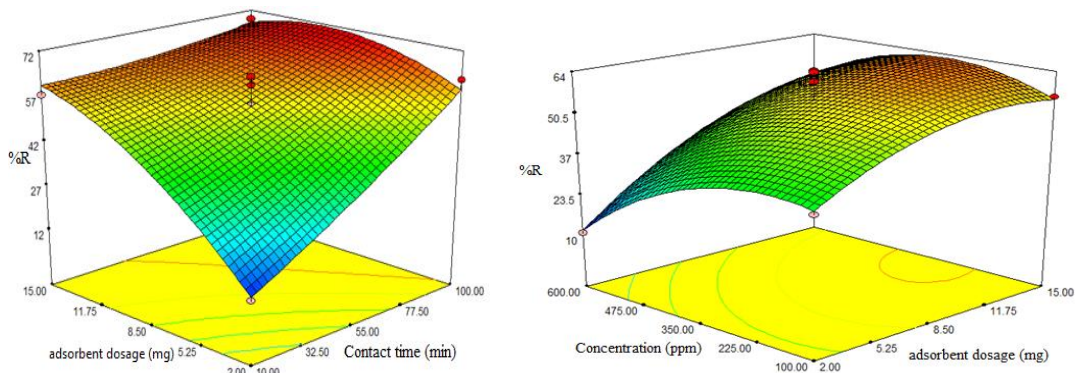


Figure 7. 3D surface plots describing the response surface for percentage remove Co(tsPc)⁻⁴ as function of a) adsorbent dosage (mg) and contact time (min) b) concentration (ppm) and adsorbent dosage(mg)

4. Conclusion

In the present study, γ -Alumina was synthesized by sol-gel method and was used as adsorbent for removal of $\text{Co}(\text{tsPc})^{-4}$ from the aqueous solution. The synthesized γ -Alumina was found to be amorphous and of nanosize. The adsorption data obtained in the batch study were well fitted to Langmuir isotherm. It was found that monolayer adsorption takes place in this process. First order and pseudo second order rate constants were found out using first order and pseudo second order rate equation. In order to study the effect of variables statistical techniques such as Box-Behnken design (BBD) was employed. The obtained results from ANOVA showed that the most significant factors affecting the removal of $\text{Co}(\text{tsPc})^{-4}$ were adsorbent dosage and contact time, respectively.

Based on the above discussion, it can be concluded that γ -Alumina synthesized by sol-gel combustion method could be used to remove $\text{Co}(\text{tsPc})^{-4}$ from aqueous solution.

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