Adsorption Studies of Cobalt (II) Complex By Bentonite clay surface

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Abstract. This paper is summarized with one of the applications of adsorption behavior; A UV-Vis method has been applied to survey the isotherm of adsorption. Results for experimental showed the applicability of Langmuir equation. The effect of temperature on the adsorption of cobalt (II) Complex by bentonite surface was studied. The results shown that the amount of adsorption was formed to increase, such as the temperature increase (Endothermic process). Cobalt (II) Complex has adsorption studies by bentonite surface at different pH values (1.6-10); these studies displayed an increase in adsorption with increasing pH. ∆G, ∆H, and ∆S thermodynamic functions of the cobalt (II) Complex for their adsorption have been calculated.

Keywords: Adsorption, Langmuir, cobalt (II) Complex, ethanol, bentonite.

1. Introduction

Heavy metals have a high effect on plants, animals, and public health. Heavy metals are also more toxic than other metals [1]. Harmfulness of heavy metals is a part of being dangerous for living organisms when overdoing the particular limits. The existence of heavy metals in nature may be influence biodegraded, producing health problems for animals, plants, and humans [2,3].

Inorganic waste of the industries always has heavy metals like Co, Ni, Cu, Zn, and Cd, etc., which tend to collect in the chain for food [4]. That is related to their high solubility in the aquatic medium, as well as; toxic metals can be adsorbed by living organism. When these metals come into the food chain for one time which it may be concentrate and collect in the human body [5].

The removal of toxic metals, like cobalt, from wastewater, is fundamental and good for human health and the environment. Sharp effects of acute cobalt injuring on humans life which can contain (asthmatic symptoms and harm for heart, thyroid, and liver). At higher concentrations of (cobalt), it
may be too caused (genetic mutations in living cells), accenting the requirement for increasing consciousness of the problems related to cobalt toxicity [6]. The removal processes of metal, such as adsorption, it is too important. This process is inexpensive, simple, and more active than the other techniques, like (solvent extraction, electrolytic processes, chemical precipitation, ion-exchange, membrane separation, reverse osmosis, or biological systems) [7]. The molecule formula of bentonite is (Mg$_2$Al$_{10}$Si$_{24}$O$_60$(OH)$_{12}$[Na, Ca ]), [8]. In this paper, we have examined the probability of the adsorption of various concentrations of cobalt (II) complex on to (bentonite) clay surface in various (pH solution), and the various temperature was studied.

2. Materials & Methods

2.1. Synthesis:

2.1.1. Synthesis of the ligand [(H$_2$L)[4-(5,5-dimethyl-3-oxocyclohex-1-enylamino)-N-(5-methylisoxazol-3-yl) benzene sulfonamide].

The preparation of the ligand (H$_2$L) was carried out according to the published procedure in literature [9], by fusing of sulfamethoxazole and dimedone at (140) °C for 1/2 hour.

2.1.2. Synthesis of cobalt (II) Complex [Co(H$_2$L)(HA)]

The metal solution of CoCl$_2$.6H$_2$O (0.061g,0.26mmole) was dissolved in (10) ml ethanol, and it was stirred for ten minutes. The H$_2$L ligand solution (0.1g, 0.026mmole) in (10) ml ethanol after accustomed for pH=8 using few drops of KOH solution was added to the metal solution. Finally, a solution of 3-amino phenol(HA) (0.03g,0.027mmole) in (10) ml ethanol was also added to the above metal solution. These results of the mixture were heated under reflux for (3) hrs. After that, the mixture was filtered. However, the precipitate was washed with an extra of ethanol and dried at room temperature for twenty-four hours. A bluish-green solid was acquired. Weight (0.13 g), yield (93.5%), m.p (>350 C°) dec. The synthesis route of the complex is shown in Figure 1. The microanalysis of results for the complex and some of its physical properties is given in Table 1.

![Figure 1. A proposed structure of cobalt (II) Complex](image)

Table 1. Microanalysis results and some physical properties for the cobalt(II) Complex

| Empirical Formula | M.wt  | Color       | M.P (°C) | M $\_\text{Found, (Calc)\%}$ | Yield % | $\lambda_\alpha$ S.cm$^2$ (molar$^{-1}$) |
|------------------|-------|-------------|----------|-----------------------------|---------|-----------------------------------------|
| [Co(H$_2$L)(HA)] | 556.52| Bluish green| 112      | 9.98 , (10.59)              | 93.5    | 17.02                                   |

M.P= melting point, Calc=calculated, M.wt = molecular weight,

2.2. Preparation of Clay Powder:
Bentonite clay sample having the (montmorillonite mineral). It was used as an adsorbent; it was obtained from (The General Company for Geological Survey and Mining, Baghdad, Iraq). Bentonite dried in an oven for 4 hours at 200°C. The clay was ground and sieved by using (0.75 mesh). The results are listed in Table 2.

Table 2. the chemical analysis of bentonite

| Constituent | SiO$_2$ | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | MgO | Na$_2$O | SO$_3$ | Losson ignition |
|-------------|---------|-------------|------|-------------|------|---------|-------|----------------|
| Wt %        | (54.66) | (14.65)     | (4.77) | (4.88)      | (6)  | 0.65    | 1.2   | 13.06          |

2.3. Preparation of Solutions:

2.3.1. Standard Stock Solution of cobalt (II) Complex solution (100 mg/L)
A standard stock solution of cobalt (II) Complex (100mg/L) was prepared by dissolving (0.01g) of [Co(H$_2$L)(HA)] in (3mL) of ethanol. The volumetric flask (100mL) was completed to the mark with an ethanol solvent.

2.3.2. Calibration Curve:
Cobalt (II) Complex solution of different concentration was prepared as mentioned in (3-4) by serial dilution absorbance values of these solutions were measured at the specified ($\lambda_{max} = 477$ nm, value for cobalt (II) Complex and plotted versus the concentration values as in Figure (2). These results were treated by (Least Square method). Concentration (2.5-100 mg / L) that obeys Beer- Lambert's law was then used in subsequent quantitative estimation of the concentration. Quantities of cobalt (II) Complex adsorbed were determined by Visb-spectrophotometric technique.

![Figure 2, Calibration curve of cobalt (II) Complex solution](image)

3. Results and Discussion
The synthesized cobalt (II) Complex [Co(H$_2$L)(HA)] has been characterized by FT-IR, (C.H.N), UV-Vis spectroscopic methods[10-12], [IR spectra of complex exhibited hands with convenient shifts due to complex figuration table (3) and (U.V-Vis) spectrum for the complex, Table 4 and Figure 3.

Table 3. FT-IR spectral data (wave number $\nu$) cm$^{-1}$ of the cobalt(II) Complex

| COMPOUND | $\nu$(OH) PHENOL | $\nu$(NH$_2$) | $\nu$(S-NH) | $\nu$(C-NH) | $\nu$(C=O) | $\nu_{as}$(S=O) | $\nu_{as}$(S=O) | $\nu$(CO–N) | $\nu$(CO–O) |
|----------|------------------|---------------|--------------|-------------|------------|----------------|----------------|-------------|------------|
| [H$_2$L] | –                | –             | 3302         | 3205        | 1612       | 1571          | 1363           | 1137        | –          | –          |
Table 4. Electronic spectral data of the cobalt(II) Complex

| COMPOUND | WAVENUMBER Nm | εMAX MOLAR-1 CM-1 | ASSIGNMENT | SUGGESTED STRUCTURE |
|----------|---------------|-------------------|-------------|---------------------|
|         | 268           | 37313             | 1425        | L.F                 |
| [CO(H₂L)(HA)] | 353          | 28328             | 1897        | L.F                 |
|         | 477           | 22371             | 1985        | C.T                 |
|         | 613           | 16313             | 685         | ⁴A₂→⁴T₂ (F)         |
|         | 679           | 14727             | 913         | ⁴A₂→⁴T₁ (F)         |

Figure 3. Spectrum of cobalt(II) Complex solution shows λmax at(477) nm

3.1. Effect of shaking time on equilibrium adsorption system

The time that is sufficient for the adsorption operation to reach equilibrium at 25 °C, Cᵢ = 50 mg/L and Particle size = 75 µm has been studied. Table (5) shown the time intervals needed for each pair of adsorbent – adsorbant to attain equilibrium.

Table 5. Equilibrium time for each adsorbent – adsorbant pair

| Cᵢ (mg/L) | Time (minute) | Cₑ (mg/L) | Equilibrium Time (minute) |
|-----------|---------------|-----------|----------------------------|
| 50        | 15            | 15.29     |                            |
|           | 30            | 11.92     |                            |
|           | 45            | 10.69     |                            |
|           | 60            | 10.67     |                            |
|           | 75            | 11.68     |                            |
|           | 90            | 11.68     |                            |
|           | 120           | 11.68     |                            |

3.2. Adsorption of cobalt (II) Complex [Co(H₂L)(HA)]
The adsorption cobalt (II) Complex from ethanol solution on bentonite has been studied initially at room temperature (25°C) as well as at (10, 37.5 and 50°C). Table 6 shows the related results by the first concentration of cobalt (II) Complex, the equilibrium concentration (C_e), and the quantity adsorbed on clay (Q_e). The results show an increase in adsorptive capacities of the clay as the concentration of cobalt(II) Complex increased until reaching a limited value [13].

### Table 6. Adsorption values of cobalt (II) Complex on bentonite surface at various temperatures

|     | 10°C | 25°C | 37.5°C | 50°C |
|-----|------|------|--------|------|
| C_e (mg/L) | C_e (mg/g) | C_e/Q_e (g/L) | C_e (mg/L) | C_e (mg/g) | C_e/Q_e (g/L) | C_e (mg/L) | C_e (mg/g) | C_e/Q_e (g/L) |
| 5   | 0.0211 | 0.1659 | 0.127185 | 0.081227 | 0.1766 | 0.1607 | 1.098942 | 0.6114 | 0.1462 | 4.181943 |
| 10  | 0.5298 | 0.3156 | 1.678707 | 0.0679 | 0.3311 | 0.205074 | 0.3941 | 0.3201 | 1.231178 | 0.7744 | 0.3075 | 2.518374 |
| 15  | 2.1603 | 0.4279 | 5.048609 | 0.6282 | 0.479 | 1.311482 | 0.9987 | 0.4796 | 2.08236 | 2.0027 | 0.3999 | 5.008002 |
| 20  | 3.7635 | 0.5412 | 6.953991 | 1.5941 | 0.6135 | 2.59837 | 2.1875 | 0.5937 | 3.684521 | 3.6821 | 0.5439 | 6.769811 |
| 25  | 5.8016 | 0.6399 | 9.066417 | 3.2364 | 0.7254 | 4.461538 | 3.2744 | 0.7241 | 4.522027 | 5.4755 | 0.6508 | 8.413491 |
| 30  | 8.1611 | 0.7279 | 11.21184 | 5.0701 | 0.8309 | 6.101938 | 4.7146 | 0.8428 | 5.593972 | 6.9429 | 0.7685 | 9.034353 |
| 35  | 9.8854 | 0.8371 | 11.8091 | 7.1321 | 0.9289 | 7.678006 | 5.8288 | 0.9723 | 5.994858 | 8.6548 | 0.8781 | 9.856281 |
| 40  | 11.3862 | 0.9537 | 11.93897 | 9.2114 | 1.0262 | 8.976223 | 7.4222 | 1.0792 | 6.877502 | 10.0951 | 0.9968 | 10.12751 |
| 45  | 12.7635 | 1.0412 | 12.25845 | 10.8016 | 1.1399 | 9.475919 | 8.9733 | 1.2142 | 7.390298 | 11.6441 | 1.1118 | 10.4732 |
| 50  | 14.4972 | 1.1834 | 12.25046 | 12.6821 | 1.2439 | 10.19543 | 10.6114 | 1.3129 | 8.082413 | 13.6005 | 1.2133 | 11.20951 |

3.3. Adsorption Isotherm

In Figure (4) the general shape of cobalt (II) Complex adsorption isotherms, when (Q_e) is a function to (C_e) among (10- 50 °C). The isotherm of cobalt (II) Complex on bentonite consistent with shape (L1- type) on (Giles classification). The isotherm of the mentioned system obeyed Langmuire equation leading to the assumption of high adsorption affinity between the cobalt (II) Complex and the clay surface in addition to the formation of one adsorption layer of cobalt (II) Complex on the clay surface[14]. The data of experimental adsorption were applied to both the empirical Freundlich equation and the theoretical Longmuir isotherm equation. These results indicated the applicability of Longmuir isotherm as shown by the linear relationship of \( \frac{C_e}{Q_e} \) versus \( C_e \), Figure (5). The Langmuir constant empirical values (Q_max) (maximum adsorption capacity), (K_a) (energy of adsorption), and correlation coefficients of cobalt(II) Complex by bentonite surface was obtained from the linear equation at different temperatures. The values are summarized in Table 7. The results showed that the maximum adsorption capacity (Q_max) of cobalt(II) Complex by bentonite (increased when temperature increase), showing that (Q_max) enhanced at higher (T). The energy of adsorption (K_a) is enhanced (10 and 25 °C) more than (37.5 and 50 °C) by bentonite surface[15-16].
Figure 4. Adsorption isotherm of cobalt (II) Complex on bentonite surface at various T

Figure 5. The linear form of Langmuir isotherm of cobalt (II) Complex on bentonite surface at different temperatures

Table 7. The Langmuir constant empirical values and the correlation coefficients for the adsorption of cobalt (II) Complex by bentonite surface at different temperatures

| Temperature (°C) | Qmax (mg/g) | Ka (L/g) | R²  |
|-----------------|-------------|---------|-----|
| 10.0            | 1.2153      | 0.3215  | 0.8752 |
| 25.0            | 1.2235      | 0.8288  | 0.9586 |
| 37.5            | 1.4830      | 0.4087  | 0.9468 |
| 50.0            | 1.6246      | 0.1598  | 0.9034 |

3.4. Effect of temperature on adsorption

The effect of temperature on the adsorption extent of cobalt (II) Complex by bentonite has been studied. Table (6) and Figure (4) illustrate data and general shapes of cobalt (II) Complex adsorption at (10, 25, 37.5, and 50 °C). The results showed an increase in the amount of cobalt (II) Complex adsorbed by bentonite with increasing temperature. Hence the adsorption process appeared endothermic. This means the interaction between bentonite and the cobalt (II) Complex requires appreciable energy in order to take place [17]. Endothermic cobalt (II) Complex uptake may also be explained as a result of probable (absorption process), in which the ions diffuse inside the crystal lattice of the clay and (the diffusing speed increase with increasing of temperature). (This behavior referred to the absorption process, which means that the absorption process may come accompanied by an adsorption process) [18]. It can also explain the increase in the amount of cobalt (II) Complex adsorbed by bentonite with increasing temperatures according to the effect of temperature on the weak bonds between the
clay platelets. Bentonite is consist of three platelets of aluminum–silicate connect to one another by weak bonds, so the increase in the temperature may be broken these weak bonds that lead to a change in the geometry of the pore of the clay, causing an increase in adsorption extent as a result of an increase in surface area of the clay [13]. The study of the temperature effect on adsorption of cobalt (II) Complex by bentonite will help in evaluating the basic thermodynamic function Free energy (ΔG), Enthalpy (ΔH), and Entropy (ΔS) of the adsorption process.

The change in free energy (ΔG°) could be determined from the equation [19].

\[ ΔG^o = -RT\ln K \]  
(1)

Where
- ΔG°: the standard free energy of change (K.J.mole⁻¹).
- R: the gas constant (8.314 J.mol⁻¹.deg⁻¹).
- K: the thermodynamic equilibrium constant [20].
- \( \frac{Q_e}{C_e} \): the maximum value of the equilibrium concentration (Ce) (mg of adsorbate per liter of solution).
- Ce: the equilibrium concentration of the adsorbate expressed in (mg) per one liter of solution.

The heat of adsorption (ΔH°) may be obtained from the equation [20].

\[ \ln K = \frac{-ΔH}{RT} + \text{Constant} \]  
(3)

The change in entropies (ΔS°) was calculated from the Gibbs equation:

\[ ΔG^o = ΔH^o – TΔS^o \]  
(4)

Table (8) gives K values at different temperatures plotting (lnK) versus (1/T) should produce a straight line with a slope = (-ΔH/R) as shown in Figure (6). Table (9) shown the basic thermodynamic values of cobalt (II) Complex adsorption by bentonite surface at different temperatures. The positive values of (ΔH°) indicate the endothermic nature of the process while the positive (ΔS°) corresponds to increase the disorder of the system increase, the negative values of (ΔG°) confirm the feasibility of the process and the spontaneous nature of sorption][8].

| Ce (mg/L) | T(°C) | T(K) | 1/T (K⁻¹) | Qe (mg/g) | Equilibrium constant (K) | ln Qmax | LnK |
|---|---|---|---|---|---|---|---|
| 10.6 | 10.0 | 283.0 | 0.003534 | 0.96 | 72.4528 | -0.0408 | 4.2829 |
| | 25.0 | 298.0 | 0.003356 | 1.12 | 84.5283 | 0.1133 | 4.4370 |
| | 37.5 | 310.5 | 0.003221 | 1.32 | 99.6226 | 0.2776 | 4.6013 |
| | 50.0 | 323.0 | 0.003096 | 1.08 | 81.5094 | 0.0769 | 4.4007 |

| ΔG° (kJ.mol⁻¹) | ΔH° (kJ.mol⁻¹) | ΔS° (J.mol⁻¹.K⁻¹) |
|---|---|---|
| -8.7237 | + 2.3559 | + 39.1471 |
| -10.2541 | | + 42.3154 |
| -10.3499 | | + 40.9204 |
| -10.3335 | | + 39.2860 |
3.5. **Effect of pH on the adsorption**

The effect of pH on the adsorption of cobalt (II) Complex with the clay (bentonite) in different media (pH = 1.6–10) has been studied using a fixed concentration at 25°C. Figure (7) demonstrates the influence of pH on the adsorption.

The results showed an increase in adsorption quantities of cobalt (II) Complex on clay surface with increasing pH values of the solution. The amount of absorbent material is low in the acid medium and then increases in the base medium. This was due to the fact that the complex was unstable in the strong acid circles. The complex tends to decompose and thus reduces the amount of adsorption. In the base medium, the complex was stable, and thus the amount of adsorption increases (the surface becomes saturated) [13].

![Figure 6](image_url)

**Figure 6.** Plot of ln K against reciprocal absolute temperature for adsorption of cobalt (II) Complex by bentonite surface

![Figure 7](image_url)

**Figure 7.** Effect of pH on adsorption of cobalt (II) Complex by bentonite surface at 25°C
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