

# Sorption of Cobalt (II) Ions from Aqueous Solutions Using Chemically Modified Chitosan

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## Abstract

Removal of Co(II) ions from aqueous solutions using chitosan-vanillin (polymer I) and chitosan-ortho-vanillin (polymer II) adsorbents has been investigated under different experimental conditions. The effect of pH, contact time, adsorbent mass, temperature, and initial concentration of studied ion on the sorption process has been studied using batch experiments. The quantity of residual ion has been estimated via atomic absorption spectrometry. The highest removal of Co(II) ions has been achieved at pH 4 with a maximum removal of 93.2% of ions after two hours of agitation. Langmuir isotherm model represents the best fit for the experimental data; whereas the highest chelation capacity was 5.899 mg g<sup>-1</sup> and 7.651 mg g<sup>-1</sup> for polymers I and II, respectively. Results from this study imply that chemisorption is the rate-determining step and thermodynamic parameters indicate that the uptake process is spontaneous and endothermic in nature.

**Keywords:** chitosan-vanillin resins, chelating polymers, sorption, wastewater treatment, cobalt removal

## 1. Introduction

Heavy metals such as Cd, As, Hg, Pb, and Co, cause pollution to the aquatic environment and pose health hazard to human health. These toxic metals can be easily absorbed by living organisms and find their way to the human body. In case these metals being consumed, they can easily cause diseases and adverse health effects (Apostoli and Catalani 2011; Jaishankar *et al.*, 2014).

A challenging problem is the low concentration of the toxic metal ions found in aqueous media. Accordingly, separation of metal ions from wastewater is complicated by several factors including pH, competing ions, and the presence of organic substances. Several methods such as "filtration, electrodialysis, ion exchange, adsorption and precipitation" have been used as effectual ways for removing toxic metal ions from aqueous systems (Fenglian and Wang, 2011; Pillai *et al.*, 2013; Zouboulis *et al.*, 2011).

Recently, some plethora approaches have been taken into consideration to improve the cheapest and effective technologies, in order to improve the quality of wastewater. Adsorption approach has been used as an alternative treatment and in recent years, the search for reasonable and affordable adsorbents has been maximized and intensified (Barakat, 2011). Biosorption refers to using biological substances as adsorbents, and this technique has been efficiently used and studied for the treatment of wastewater containing heavy metals (Dixit *et al.*, 2013; Witek-Krowiak *et al.*, 2011). Seaweeds, molds, yeasts, bacteria, and crab shells, among other kinds of biomass, have been tested for metal biosorption with very encouraging results.

Chitosan is considered as semi-synthetically derived amino polysaccharide that has a unique structure with high sophisticated functionality, multi-dimensional properties, and a wide range of applications in biomedical and other areas. In the last two decades, many significant studies have been reported and carried out on chitosan and on its potential use in various bioapplications (Bhattari *et al.*, 2010; Jayakumar *et al.*, 2010; Prabhu and Meenakshi, 2014). Chitosan is utilized as a natural biosorbent for toxic metal ions. This advantage can be ascribed to the large number of hydroxyl groups in chitosan, existence of primary amino groups which are considered as sorption sites, and flexibility of polymer chain structure that is suitable for complexing with metal ions (Inoue *et al.*, 1999). Regardless of these features, chelation capacity is still limited to the degree of deacetylation, nature of the metal ion, and pH of the solution. For this reason, chitosan has been modified to be able to overcome these limitations. Some of these modifications have been achieved by reaction with the amines (Zalloum *et al.*, 2008) or through the reaction with hydroxyl groups of the glucosamine unit in chitosan. A large number of chitosan derivatives have been obtained with the aim of adsorbing metal ions by grafting new functional groups on the chitosan backbone. The integration of the new functional groups is very important and significant in increasing the density of

sorption sites. It is also important to change the pH range for metal sorption and to change the sorption sites to be able to increase sorption selectivity for the target metal (Shukla *et al.*, 2013). Various studies have been carried out in the field of chitosan-based sorbents, and novel resins with enhanced chelation capacities for the target species in aqueous solutions and with greater stability and reusability have been synthesized (Jana *et al.*, 2011; Emara *et al.*, 2011; Wu *et al.*, 2010; Crini *et al.*, 2008; Krishnapriya and Kandaswamy, 2009; Wang and Chen, 2014; Kolodynska, 2011; Dinu and Dragan, 2010; Liu *et al.*, 2013; Maleki *et al.*, 2015, Rocha *et al.*, 2016). In this respect, vanillin is also considered as a biomass compound that plays a significant role as a renewable feed stock (Amarasekara and Razzaq, 2012). Moreover, *ortho*-vanillin as a related compound was utilized in organometallic polymers, where a Schiff base was derived from *ortho*-vanillin which chelates other metal ions (Kaya *et al.*, 2008).

Cobalt (II) compounds are important in several industrial purposes. They can be utilized in different applications such as; nuclear power plants, metallurgy, mining, pigments, paints and electronic tools (Baun and Christensen, 2004; Babel and Krniavan, 2003). Cobalt (II) ions are usually found in industrial effluents such as acid mine sewerage and urban wastewater treatment plant. The existence of cobalt ions in wastewaters demonstrates major environmental problems. Cobalt ions are toxic and not biodegradable and are being responsible for numerous types of health issues in animals, plants and human beings (Muzenda *et al.*, 2011; Abdulkareem *et al.*, 2013). Consequently, it is very important to manage the concentration of cobalt ions in wastewater before its discharge into the aquatic systems.

In this paper, we report on the chelation properties of two synthesized sorbents; chitosan-vanillin (polymer I) and chitosan-*ortho*-vanillin (polymer II) toward Co(II) ions from aqueous solutions. Equilibrium studies, sorption isotherm models, kinetic and thermodynamic parameters were investigated. The obtained polymers could be used as adsorbents for wastewater treatment.

## 2. 2. Materials and methods

### 2.1. Materials and Instruments

Unless otherwise indicated all chemicals were obtained from commercial sources and were used as received. Vanillin (99%) (Alfa Aesar), *ortho*-vanillin (99%) (Chem Cruz), Sodium acetate anhydrous (99%) (UFC Biotechnology), Glacial acetic acid (99%) (Sigma-Aldrich), Chitosan (not less than 85% glucosamine) with medium molecular weight (RxBiosciences), Cobalt (II) acetate tetrahydrate (99%) (Sigma), Ethanol (99%) (AnalaR), Acetone (99%) (AnalaR), Methanol (99%) (AnalaR). Orbital Shaker (Steady Shake, 757), Atomic Absorption Spectrophotometer (Shimadzu, AA-7000), pH meter (Metrohm, 525A) were utilized for accomplishing experimental works. Thermal Gravimetric Analysis (temperature range from 10 to 600 °C) (Exstar, TG/ DTA 7300), FTIR (IRAFFINTT-2), SEM (INSPECT S50) were used for characterization studies.

### 2.2. Synthesis of Chitosan-Vanillin Resins; Polymers I-II

Polymers I and II were synthesized according to procedures (Wang *et al.*, 2003; Alakhras *et al.*, 2018) which involved refluxing 5.7 g of chitosan with 90 mmol of a vanillin derivative for each polymer (vanillin for polymer I and *ortho*-vanillin for polymer II) in 90 mL of methanol and 9 mL of glacial acetic acid for 10 h. The poly Schiff bases obtained were collected by filtration and washed with ethanol and acetone, respectively. These polymers were purified by soxhlet extraction with acetone and then with ethanol for 24 h, and the solid polymers (Beige for polymer I, yellow for polymer II) were dried in an oven at 70 °C for 24 h.

### 2.3. Preparation of Buffer solutions

A series of acetate buffer solutions were prepared from sodium acetate and acetic acid to obtain pH values ranging from 3.0 to 7.0 and checked with pH meter.

### 2.4. Preparation of metal ion solutions

A Stock solution of metal ion with a concentration of 1000 mg L<sup>-1</sup> was prepared by dissolving the appropriate amount of metal salt in deionized water. Metal ion solutions with (1, 3, 5, 10 and 15) ppm were prepared from the stock solution in deionized water as well.

### 2.5. Removal of Co (II) ions onto the polymer materials

The sorption behaviour of the two resins has been investigated by the batch equilibrium method. Briefly, 0.05 g of adsorbent was suspended in a 100 mL Erlenmeyer flask containing 25.0 mL of a buffer solution with pH ranging from 3.0 to 7.0 for a period of 2 h with continuous shaking to equilibrate. Then, 25.0 mL of 15 mg L<sup>-1</sup> of a Co(II) solution was added, and mixtures were shaken at 30 °C. To evaluate the effect of time on the metal ion uptake, similar experiments were performed using different time intervals (5, 10, 20, 30, 60, 120, 240, 480, and 1440 s). Thereafter, each sample was filtered and the concentration of residual metal ions was determined with the aid of a flame atomic absorption spectrophotometer (FAAS). Similar experiments were carried out using different metal ion concentrations (1, 3, 5, 10, and 15) mg L<sup>-1</sup> at different temperatures of (30, 50, and 70 °C). In a similar fashion, the effect of polymer mass has also been investigated by using different amounts (0.01, 0.05, 0.1, 0.2, and 1.0 g) of dry resins and applying the optimal conditions of contact time and pH on metal ion uptake.

At equilibrium, the amount of metal ion adsorbed,  $Q_e$  (mg metal ion / g polymer), was evaluated using the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium (after 24 h) concentrations of metal ions in the liquid phase (mg L<sup>-1</sup>), respectively,  $V$  is the volume of solution (L), and  $W$  is the mass of dry resin used (g). For the sorption experiments, the value of metal ion chelated at several intervals was also studied using the formula:

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where,  $C_t$  ( $\text{mg L}^{-1}$ ) is the metal ion concentration in solution at different periods of time “ $t$ ”.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of polymers

Schiff base materials containing an imine group are normally formed by condensation of a primary amine and an active carbonyl group. In this study, chitosan acts as the primary amine that reacts with either vanillin to afford polymer I or with *o*-vanillin to form polymer II as shown in Fig. 1.

Detailed analyses of IR spectra, TGA, SEM, and BET surface area of the obtained chelating materials can be found elsewhere (Alakhras *et al.*, 2018). Formation of imine ( $\text{C}=\text{N}$ ) group was confirmed by IR spectra and appeared between  $1630\text{--}1640\text{ cm}^{-1}$  (Shukla *et al.*, 2013).

Furthermore, IR spectra of the two  $\text{Co(II)}$ -loaded polymers revealed that imine and hydroxyl bands became sharper

with less intensity and shifted to lower frequency, indicating that the binding with  $\text{Co(II)}$  ions occurs through these sites. TGA investigation showed that the synthesized polymers have higher degradation temperatures than pure chitosan which may suggest that the presence of an imine group along with phenolic aromatic rings improve the thermal stability of the new modified chitosan polymers and results in more rigid structures

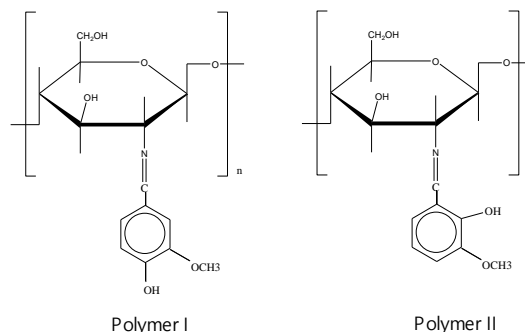


Figure 1. Structures of Polymers I and II

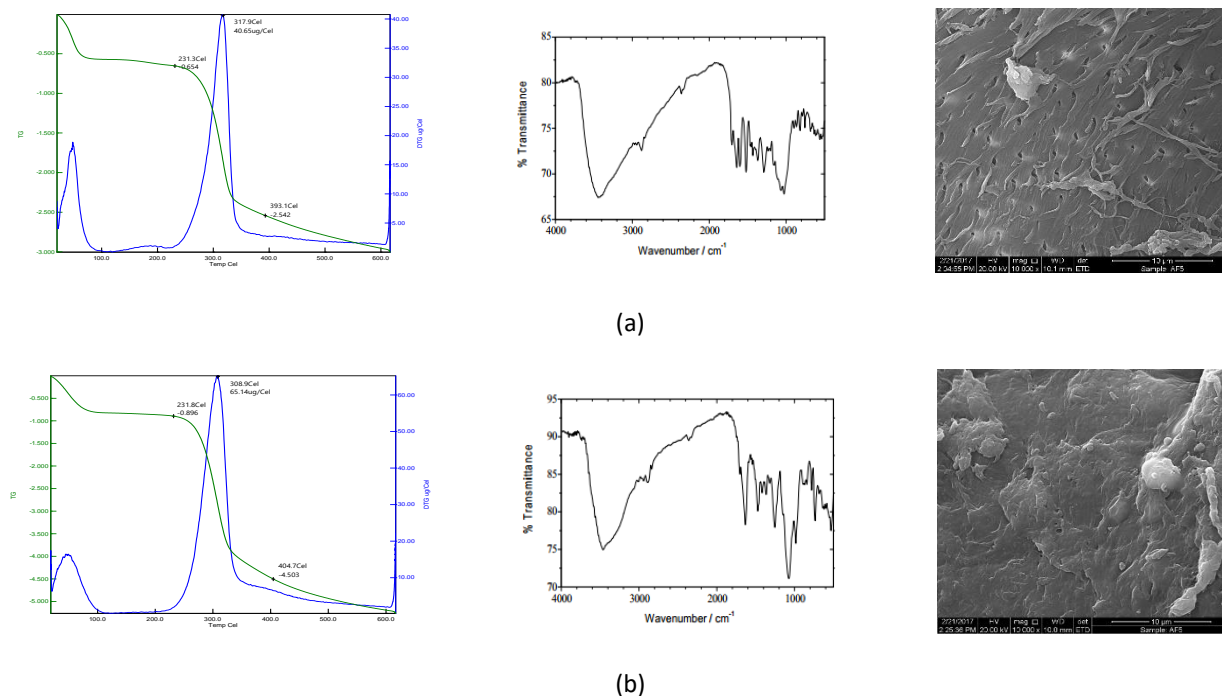


Figure 2. FTIR, TGA and SEM characterizations of (a) polymer I and (b) polymer II

SEM micrographs of polymers I and II reveal that the surface morphology of  $\text{Co(II)}$ -loaded polymers had been altered by adsorption of  $\text{Co(II)}$  ions from cracked to nearly smooth surfaces, which indicates that sorption of heavy metal ions is a result of strong chemical interactions between the polymers active sites and metals ions (Al Hamouz, 2016).

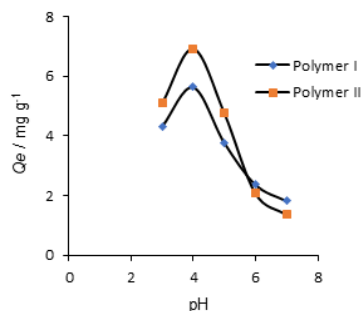
#### 3.2. Effect of pH on $\text{Co(II)}$ Uptake

Shown in Figure 3 are results of the effect of pH on the sorption of  $\text{Co(II)}$  ions onto polymers I and II. Results reveal

that the best adsorption capacity for the two polymers was achieved at pH 4.0 and decreases with as the pH increases.

The principal types of  $\text{M(II)}$  ions in aqueous system, for instance:  $\text{M}^{2+}$ ,  $\text{M(OH)}_2$ ,  $\text{M(OH)}_3^-$  and  $\text{M(OH)}_4^{2-}$ , depend on the pH of solution. At higher pH values, deposition of metal hydroxide  $\text{M(OH)}_2$  plays a principle role in decreasing metal ions uptake by adsorption (Negm *et al.*, 2015). Ionic species in acidic solution are specifically found with two or three positive charges ( $\text{M}^{2+}$  and  $\text{M}^{3+}$ ). At low pH values,  $\text{Co(II)}$  ions can compete favourably toward binding sites compared with hydrogen ions. Nevertheless, at high pH values the solution can turn into an oxide which has no charge and its

interaction can be decreased noticeably by adsorbents (Ramos *et al.*, 2002). The removal percentage of Co(II) ions ranged between 43.5 and 12.2 % for polymer I, and between 7.5 and 46.2 % for polymer II which were still considered low in comparison with other metal ions.



**Figure 3.** Effect of pH on Co(II) adsorption by two polymers I and II ( $C_0 = 15 \text{ mg L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ ,  $W = 0.05 \text{ g}$ ,  $V = 0.05 \text{ L}$ , Time = 2 h)

**Table 1.** Adsorption of Co(II) on polymers I and polymer II at different concentrations

$C_0$ (mg L <sup>-1</sup> )	Polymer I			Polymer II		
	$C_e$ (mg L <sup>-1</sup> )	$Q_e$ (mg g <sup>-1</sup> )	R%	$C_e$ (mg L <sup>-1</sup> )	$Q_e$ (mg g <sup>-1</sup> )	R%
1	0.232	0.767	76.72	0.340	0.659	65.98
3	1.225	1.774	59.16	1.358	1.642	54.74
5	2.246	2.753	55.07	2.283	2.716	54.33
10	5.658	4.342	43.42	5.688	4.312	43.13
15	10.168	4.831	32.21	9.630	5.369	35.79

These results can be explained by the following: at the same mass of adsorbent, a higher concentration of Co(II) ion leads to occupying more binding sites on the surface of both polymers, in comparison with lower initial concentrations. Similarly, a higher initial concentration increases the driving force in order to overcome the mass transfer resistance of Co(II) ions between the aqueous and solid phases. This can lead to a higher chance of collision between the Co(II) ions and the surface of each polymer. Furthermore, increasing uptake capacity with increasing initial Co(II) ion concentration may also be as the result of more intense interaction between each polymer's surface and Co(II) ions (Eser *et al.*, 2012).

Results also have showed that if the initial solute concentrations are increased, the total percent of removal is decreased. For instance, on changing the initial concentration of Co(II) from 1 to 15 mg L<sup>-1</sup>, the removal efficiency decreased from 76.72 to 32.21% for polymer I and from 65.98 to 35.79 % for polymer II. This indicates that if the concentration is low, the initial moles ratio of metal ions on the available surface area is low too, and the fractional sorption becomes independent on initial

### 3.3. Effect of initial Co(II) ions concentration and isotherm studies

During the adsorption process, the initial concentration of metal ion in solution presents the fundamental driving force which makes the system capable to overcome the mass transfer resistance over transmission of metal ions from solution to solid phase.

Listed in Table 1 are the results of our investigation on the adsorption of Co(II) onto polymers I and II. The effect of initial Co(II) ion concentration on adsorption efficiency was studied in the range of (1–15) mg L<sup>-1</sup> at pH 4 and at 2 h of agitation time using an adsorbent mass of 0.05 g. Results show that when the initial concentration of Co(II) ions goes up from 1 to 15 mg L<sup>-1</sup>, the removal capacity of these ions by polymers I and II increases from 0.767 to 4.831 mg g<sup>-1</sup> and from 0.659 to 5.369 mg g<sup>-1</sup>, respectively.

concentration. However, at higher concentrations, the available sites of sorption become fewer compared to the metal ions moles. Therefore, the percentage removal of metal would be dependent upon the initial metal ion concentration.

Experimental data of adsorption of Co(II) ions onto polymers I and polymer II were investigated by a linear plot of Langmuir, Freundlich, and Temkin isotherm models

as  $C_e/Q_e$  versus  $C_e$ ,  $\log Q_e$  versus  $\log C_e$ , and  $Q_e$  versus  $\ln C_e$ , respectively (Ibrahim and Sani 2014).

Results in Table 2 reveal that Langmuir isotherm is the most fitting and appropriate model to explain the adsorption of Co(II) with  $R^2 = 0.9867$  for polymer I and 0.9811 for polymer II. Nevertheless, the  $R^2$  values for Freundlich and Temkin isotherms are still very close to that of Langmuir model. The Langmuir data show that polymer II has more adsorption capacity with 7.651 mg g<sup>-1</sup> than polymer I with 5.899 mg g<sup>-1</sup>, and the adsorption coefficient ( $K_L$ ) value of polymer II is higher than that of polymer I which also means that the affinity of adsorption is more convenient for Co(II) ions with polymer II than polymer I (Shshmohammadi-Kalalagh *et al.*, 2011).

**Table 2.** Langmuir, Freundlich and Temkin models parameters for the adsorption of Co(II)

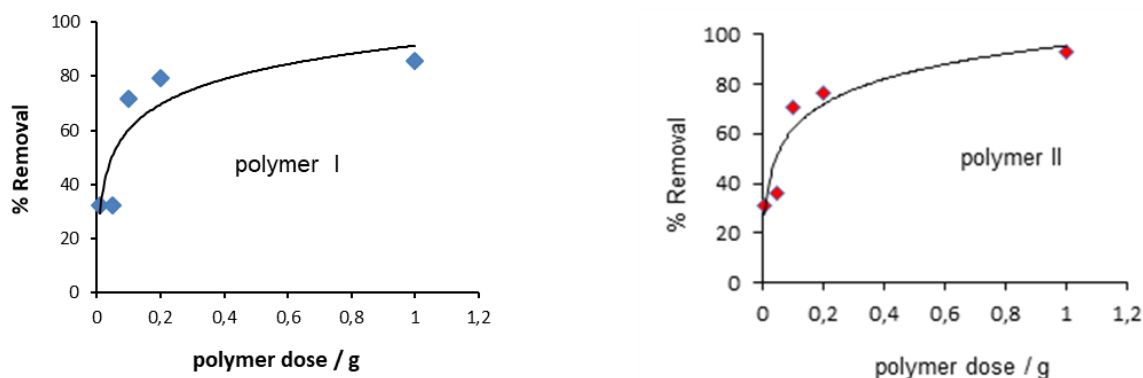
	Langmuir model					Freundlich model			Temkin model		
	$Q_0$ (mg g <sup>-1</sup> )	$K_L$ (L g <sup>-1</sup> )	$R^2$	$R_L$	n	$K_F$ (mg g <sup>-1</sup> )	$(\text{mg L}^{-1})^{1/n}$	$R^2$	B (J mol <sup>-1</sup> )	A (L g <sup>-1</sup> )	$R^2$
Polymer I	5.899	0.236	0.9867	0.130	1.967	1.659	0.9412	1.135	6.215	0.9215	
Polymer II	7.651	0.445	0.9811	0.220	1.564	1.385	0.9530	1.436	3.44	0.9129	



Depending upon the impact of the separation factor,  $R_L$ , that is represented by Equation 3 on the isotherm profile, it was indicated that the average values of  $R_L$  were between  $0 < R_L < 1$ , which revealed a reasonable sign suggesting the uptake of Co(II) ions by the two polymers is a favourable process.

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

From Table 2,  $K_F$  values, which indicate the adsorption capacity, and  $1/n$  values demonstrate the adsorption process is favourable which implies that removal of cobalt ions is encouraging, especially with polymer II. Temkin isotherm model can also be used to explain the adsorption process by the two polymers. This model assumes that the adsorption energy decreased upon increasing surface coverage with metal ions and the sorption process can be depicted by uniform distribution of binding energies up to a maximum. On the other hand, the heat of adsorption (constant B) equals 1.135 and 1.436 J mol<sup>-1</sup> for polymers I and II, respectively, whereas the maximum binding energy (constant A) equals 6.215, and 3.440 L g<sup>-1</sup>, respectively. Overall, in addition to Langmuir model, the calculated parameters of Freundlich and Temkin models also confirm that adsorption of Co(II) ions onto both polymers surfaces (Dada *et al.*, 2012) is a favourable process.



**Figure 4:** Effect of adsorbent dosage on Co(II) adsorption by two polymers. ( $C_0 = 15 \text{ mg L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ ,  $V = 0.05 \text{ L}$ , Time = 2 h)

However, as the adsorbent mass increases, the uptake capacity  $Q_e$  of metal ions for each unit of sorbent mass showed a decreasing trend. This is due to the lower utilization of adsorption sites of the sorbent at higher mass, which may result from possible overlapping or gathering of adsorption sites, leading to an increase in diffusion path and reduction of the available area for adsorption. Additionally, results show that the maximum removal of Co(II) ions was 85.9 % for polymer I and 93.2 % for polymer II at 1.0 g mass.

### 3.5. Effect of adsorption time and kinetic studies

Effect of time on the extent of adsorption is related to the stability of the complex that may form during the

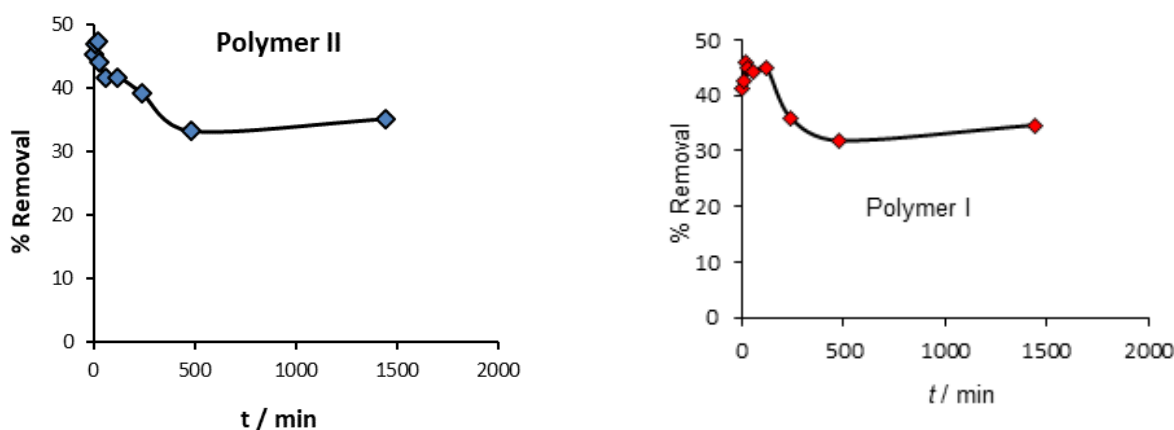
The studied biosorbents showed higher adsorption capacity toward cobalt ions compared to other sorbents. As obtained from Langmuir data, the adsorption capacity of Co(II) onto magnetic chitosan (MCS) was 2.98 mg g<sup>-1</sup> (Chen and Wang, 2012). Moreover, the maximum adsorption capability of 0.477 mg g<sup>-1</sup> of Co(II) using chitosan was reported by Padala *et al.* (Padala *et al.*, 2011). Ebner and his group (Ebner *et al.* 2001) reported that the maximum adsorption efficiency of Co(II) on magnetite was 0.111 mg g<sup>-1</sup> at pH 5.0. In addition, in a study reported by Yavuz and coworkers, which was focused on the potential removal of cobalt ions from aqueous solution by kaolinite, maximum adsorption capacity of 0.90 mg g<sup>-1</sup> was achieved (Yavuz *et al.*, 2003).

Overall, the result obtained in the equilibrium studies revealed that, comparing with other studies, our polymers are feasible as adsorbents for the removal of Co(II) metal ions from wastewater samples.

### 3.4. Effect of adsorbent mass

The effect of adsorbent mass on the removal of Co(II) ion from aqueous media is depicted in Figure 4. Results show that, as the adsorbent mass increases, the removal percentage increases due to greater availability of extra adsorption sites for metal ions (Altun and Pehlivan, 2007).

adsorption process between the metal ions and the sorbent. The more stable the metal complex is the more metal adsorption efficiency can be achieved. In this context, the effect of time was carried out with 15 mg L<sup>-1</sup> of Co(II) ion at pH 4 and at 30 °C. Other concentrations of Co(II) were examined after the intervals of (5, 10, 20, 30, 60, 120, 240, and 480 s). Figure 5 revealed that the removal percentage of Co(II) ions by polymers I and II was only between 40 and 45 % after two hours of agitation time. Then, the removal efficiency decreased significantly upon increase of time. This behaviour can be attributed to the weak complexation tendency between cobalt ions and the ligand sorbents, which is highly affected after certain time of metal chelation.



**Figure 5.** Effect of contact time on Co(II) adsorption by two polymers. ( $C_0 = 15 \text{ mg L}^{-1}$ ,  $T = 30 \text{ }^\circ\text{C}$ ,  $W = 0.05 \text{ g}$ ,  $V = 0.05 \text{ L}$ )

The Kinetic data were processed using two adsorption patterns; pseudo first-order kinetic (equation 4) and pseudo second-order kinetic model (equation 5). These models best describe the adsorption of transition metal ions onto different sorbents (Shshmohammadi-Kalalagh *et al.*, 2011).

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

Data in Table 3 show that the theoretical values of  $Q_e$ , calculated from pseudo second-order model, are closer to

the experimental values, as compared to those calculated from the pseudo first-order model. Additionally, results show that the experimental values were  $5.198 \text{ mg g}^{-1}$  for polymer I and  $5.266 \text{ mg g}^{-1}$  for polymer II. Moreover, the higher correlation coefficient ( $R^2$ ) of the pseudo second-order kinetic model implies that the experimental data were suitably fitted with pseudo second-order model as the potential form for the adsorption behaviour of Co(II) ions. Furthermore, the closeness of pseudo-second order model with the experimental data indicates the interaction of metal ion with the adsorption sites of the polymeric surfaces is the rate-determining step for the entire adsorption process.

**Table 3.** Kinetic parameters for Pseudo first-order and Pseudo second-order for the adsorption of Co(II)

	$(Q_e)_{\text{Exp}} (\text{mg g}^{-1})$	Pseudo first-order			Pseudo second-order		
		$(Q_e)_{\text{Cal}} (\text{mg g}^{-1})$	$K_1 (\text{min}^{-1})$	$R_1^2$	$(Q_e)_{\text{Cal}} (\text{mg g}^{-1})$	$K_2 (\text{g mg}^{-1} \text{min}^{-1})$	$R_2^2$
Polymer I	5.198	1.091	0.0016	0.772	4.782	0.0029	0.964
Polymer II	5.266	1.137	0.0023	0.772	5.032	0.0064	0.965

### 3.6. Effect of temperature and thermodynamic studies

Effect of temperature on the adsorption of Co(II) ions by the two polymers was examined between  $30$  and  $70 \text{ }^\circ\text{C}$ , and with an initial concentration of  $15 \text{ mg L}^{-1}$ . The adsorption process at lower temperatures was more favourable and reached a maximum at  $40 \text{ }^\circ\text{C}$ . This behaviour can be explained in terms of the weaker interaction between the metal ions and the active groups of two polymers at higher temperatures. The obvious fluctuation in removal percentage of Co(II) ions by polymer I compared with polymer II could be ascribed to the complex stability between adsorbate-adsorbent as temperature changes from  $30$  to  $70 \text{ }^\circ\text{C}$  without (Figure 6).

The values of thermodynamic parameters which include Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ) were calculated using equation 6 where  $K_L (\text{L mol}^{-1})$  is Langmuir constant and  $M_w (\text{g mol}^{-1})$  is molecular weight of the adsorbate (Tran *et al.*, 2017).

$$\ln(M_w \times 55.5 \times K_L) = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

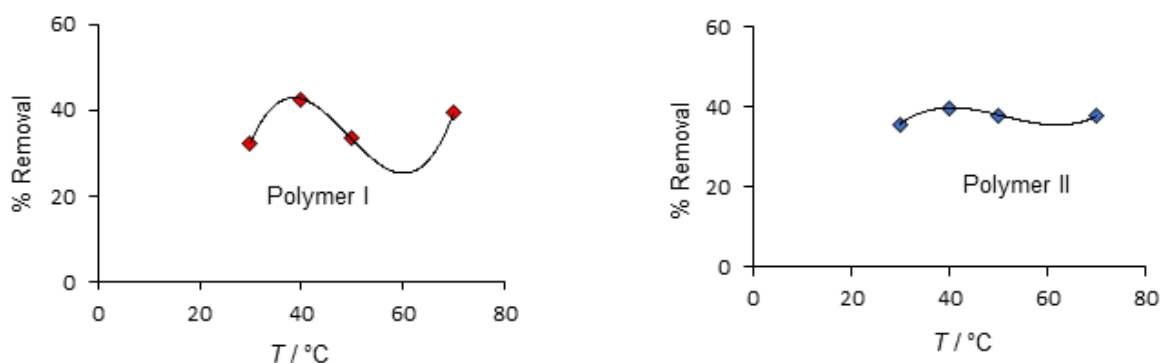
The negative sign of the Gibbs free energy change confirms that the adsorption process was fast, spontaneous, and feasible at all four temperatures. The positive values of  $\Delta H$  indicate that for both polymers the adsorption process is endothermic in nature. In addition, the positive values of  $\Delta S$  indicate that part of the affinity towards Co(II) ion comes from an increase of randomness during the adsorption of this ion onto the modified chitosan.

## 4. Conclusion

Synthesized chitosan-vanillin and *ortho*-vanillin chelating polymers have been utilized for the removal of Co(II) metal ions from aqueous solutions. The sorption process was best fitted with the Langmuir isotherm model, suggesting homogeneity of the adsorption process. Results obtained from this investigation reveal that adsorption of Co(II) ions onto polymers follows pseudo second-order kinetics,

suggesting that the process is controlled by the stage where Co(II) ions interact with sorption sites. Additionally, results show that removal of ions by both polymers was favourable, with spontaneous nature and endothermic characteristic. The highest chelation capacity obtained for

both polymers was 5.899 mg g<sup>-1</sup> for polymer I and 7.651 mg g<sup>-1</sup> for polymer II. Finally, this study indicated that our polymers are feasible as adsorbents for the removal of Co(II) metal ions from wastewater samples.



**Figure 6.** Effect of temperature on Co(II) adsorption by two polymers. ( $C_0 = 15 \text{ mg L}^{-1}$ ,  $W = 0.05 \text{ g}$ ,  $V = 0.05 \text{ L}$ ,  $\text{Time} = 2 \text{ h}$ )

**Table 4.** Thermodynamic parameters for the adsorption of Co(II) for two polymers at different temperatures

	$\Delta H \text{ (KJ mol}^{-1}\text{)}$	$\Delta S \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$	$\Delta G \text{ (KJ mol}^{-1}\text{)}$			
			$T = 30 \text{ }^\circ\text{C}$	$T = 40 \text{ }^\circ\text{C}$	$T = 50 \text{ }^\circ\text{C}$	$T = 70 \text{ }^\circ\text{C}$
Polymer I	3.716	69.10	-18.357	-20.932	-20.113	-22.663
Polymer II	9.515	93.70	-16.759	-18.613	-18.553	-19.865

#### Conflicts of Interest

Authors declare that there is no conflict of interest regarding the publication of this paper.

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