Competitive   adsorption of Co(II) in a binary and tertiary system with   metal ions Cr(III) and Ni(II) on Lewatite S-100 cation exchange resin

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Abstract: The main contribution of this study to the state of the art on the subject matter was to study the efficiency of the Lewatite S-100 in the purification of cobalt(II) ions even in conditions of   competition. The capacity removal of Co((II)   was examined   by varying experimental conditions viz. amount of adsorbent, pH of the solution and contact time. The equilibrium data have been found to fit both Langmuir and   Freundlich isotherms. The results were analyzed using three kinetic models, psendo-first, pseudo-second order and Weber-Morris intrapartical diffusion. Sorption properties of Co(II) in a binary and tertiary system with   metal ions Cr(III) and Ni(II) on Lewatite S-100 cation exchange resin were investigated in batch system.

Key Words: Lewatite S-100 cation exchange resin, Co (II) solution, Isotherm, Kinetics and competitive cations Cr(III) and Ni(II).

1. Introduction

People have used metals for many centuries and in our day the mass usage of metals in accepted as an inalienable fact. The hydrometallurgical industry produces many types of waste streams. The toxic nature of heavy metal ions, even at trace levels in natural waters, has been a puplic health problem [1]. The presence of these heavy metals in the environment is of importance concern due to their toxicity and health effects on the human and living creatures. Therefore, elimination of toxic heavy metals is attended by many researches [2]. There are various methods for the removal of heavy metals; one of the common methods for removing metals is ion exchange technique. Ion exchanges onto low-cost media a such as synthetic resins offers an attractive and inexpensive option for the removal of dissolved metals.

In recent years, a number of commercial resin such as Lewatit TP-207[3], Amberlite IR-120 [4], Amberlite IRC-748 [5], Lewatite S-100 [6], Lewatit, CNP-80 [7], Amberlite IRC-718 [8] and Lewtit Monoplus SP 112 [9] have been used to remove heavy metals from wastewater. Ion-exchange is highly effective, low-cost material, efficient, and easy to operate among the physicochemical treatment processes. Furthermore, ion-exchange is particular effective for treating water including low concentration of heavy metals which is very common in practice[10-12]. Cobalt(II) is   one of the common toxic   metals affecting the environment, is present in the wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic [13].

High levels of cobalt(II) may affect in several health troules such as paralysis, diarrhea, low blood pressure, lung irritation and bone defects [14]. The standard level of cobalt(II)   in drinking water is $2\mu gL^{-1}$, but values up to 107 μgL^{-1} have been reported [15]. With a better awareness of the problems associated with cobalt(II)   research studies related to the methods of removing cobalt(II)   from wastewater have drawn attention increasingly[16]. Studies on the adsorption of heavy metals, which exist in either an individual or mixed state, are important in determining the capacity of resins to respond to the introduction of pollutants into wastewater systems. Pollutants can generate multi-component solutions, and the competition among the heavy metals onto the resins can affect the mobility of heavy metals and the efficiency with which they can be removed from such multi-component solution. However, few studies have been reported that involve direct measurement of heavy metal competition onto an ion exchange resin in multi-component solution [17-19].

The main contribution of this study to the state of the art on the subject matter was to study the efficiency of the Lewatite S-100 in the purification of cobalt(II) ions even in conditions of competition. The parameters that influence in sorption process, such as initial cobalt(II)   concentration, contact time and pH were investigated. The sorption experiments were carried out in single, binary and ternary component system.

2- Materials and methods
2.1. Characteristics of the Lewatite S-100 cation

exchange resin.

The cation exchange resin Lewatite S-100 (M/S. Rohm and Hass corp., USA), was characterized with regard to its adsorption properties for specific heavy metals. Physical and chemical properties of the resin are shown in Table (1). The resin was washed with 2M HCl before being used to remove possible organic and inorganic impurities, it was then washed with deionized water until reaching a neutral pH for the supernatant.

2.2. Preparation of solution

Cobalt [Co(II)] was made from Analar (CoCl$_2$.6 H$_2$O) stock solution (1000 mg/L) of cobalt ion was prepared using deionized water and subsequently diluted. The pH of the solutions was adjusted using universal buffer. Ni(II) and Cr(III) ions were prepared in the forms NiCl$_2$.6 H$_2$O and CrCl$_3$.6 H$_2$O diluted in deionzied water respectively. All the chemicals used were of analytical grade and obtained from Aldrich, USA.

2.3. Apparatus

An atomic absorption spectrophotometer (AAS). Inductively coupled plasma ECP, 6500DUO, Thermoscientific England was used to analyze the concentration of Co(II) in solution in single and multi component system. The pH measurements were carried out with a glass electrode (HANNA. pH 211) model.

2.4. Batch adsorption

Batch adsorption technique was used out for the study of Co(II) adsorption from solution. The effect of contact time (20-9o min), temperature (25, 35 and 45°C), initial metal ion concentration from (2-12) mmol/l,pH's varying (2.2-10.5) and adsorbent dose (0.01-0.1g) were studied. In typical experiment, 0.05 g of adsorbent was contact with 50 ml of(8 mmol/l) of the Co(II) solution for 24 h (the time required for equilibrium to be reached between metal ion in the adsorbed phase and metal ion in solution) using a bath to control the temperature (25, 35 and 45°C). The Co(II) ion concentrations in the solutions were determined by atomic spectrophotometer (AAS).

The uptake of metal ion in solution was calculated by the difference in their initial and final concentration. The obtained data were employed to calculate the equilibrium metal uptake capacity[20] according to the Eq. (1).

$$q_e = \frac{(C_o - C_e)v}{m} \qquad (1)$$

Where q$_e$ (mg/g) is the equilibrium amount of metal in the adsorbed phase, C$_o$ and C$_e$ are the initial and equilibrium solution concentrations (mg/L), respectively, v is volume of the solution (L) and m is the mass of sorbent dose (g) in the solution.

2.5 Effect of competitive cations

Competitive equilibrium experiments were carried out by combining the 0.05 g of the corresponding adsorbent with 50 ml of Co(II) in a binary and tertiary system with metal ions Cr(III) and Ni(II) solution on Lewatite S-100 using different initial metal concentration in the range of (8 mmol/l) and stirring speed remained constant. Experimental competitive adsorption equilibrium isotherms were obtained by batch equilibrium stirring at 25°C ± 2 was kept until equilibrium when the concentration of both the metals in the solution did not show any further change. Separate competitive equilibrium experiments were carried out for adsorbent target metal, together with a competitive metal ion. Thus for Lewatite S-100 adsorbent – target metal, three competitive adsorption isotherm. In each case, the pH was fixed at the optimum one determined for the single adsorption of the target metal. Langmuir isotherm has been commonly used for predicting single and competitive adsorption of pollutants from aqueous solution onto adsorbent.

3. Results and Discussion

3.1. Effect of pH on metal uptake for single – ion solution

It is well known that solution of pH is an important factor controlling the surface charge of the adsorbent and the degree of ionization of the adsorbate in aqueous solution [21]. The effect of pH on the sorption of Co(II) ions was tested at different pH values (2.2.-10.5) using Lewatite S-100 cation exchange resin. Effect of pH on the removal efficiency is shown in Fig. (1). The results indicated that the maximum uptake of Co(II) ions occurred at initial pH of 4.5 ± 0.5. The adsorption capacity of the resin increased with increase in pH of the aqueous solution. Similar trend was observed by many earlier works with the adsorption of Co(II) from aqueous solution [22] .Co(II) adsorption capacity varied little and the sorption capacity was kept constant in the pH range (6.0-10.0). At the high pH value, decrease in removal efficiency achieved by resin, can be described with the formation of Co(OH)$_2$ during the reaction of Co(II) with OH$^-$. In this state, hydrolysis accompanied by precipitation of metal hydroxide may occur[23].

3.2. Effect of sorbent amount on adsorption

The resin amount is one of the important parameters to obtain the quantities uptake of metal ion[20]. The retention of Co(II) was examined in the relation to the amount of the resin. For this reason, amount of the resin were tested in the range of (0.01-0.1g) and equilibrated for 24 h at an initial concentration of (8 mmol/l) in 50 ml solution. The results are given in Fig. (2). It is apparent that by

increasing the resin amount, the sorption density, and the amount adsorbed metal ion per unit mass increases. It was found that the retention of metals increased with increasing amount of the resin up to 0.05 gm. This value was taken as the optimum amount for other trais. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial Co(II) concentration, because for a fixed initial solute concentration, increasing adsorbent doses provide greater surface area [18,19].

3.3. Effect of contact time

The actual rates of ion exchange can vary over a wide range, requiring a few seconds to several months to reach equilibrium[24]. Ion exchange is an equilibrium reaction that is dependent on the ionic equilibrium reaction that is dependent on the ionic concentration of various ions both inside and outside the resin bead Fig. (3). The effect of contact time on the ion exchange of Co(II) by the Lewatite S-100 resin was studied by taking 0.05g resin with 50 ml of metal ion solution with time interval(10-90) min. The experimental date indicate that Co(II) ion adsorption increased by increasing time. This is due to the higher contact between the sorbent surface and Co(II) ion. Subsequently, the adsorption is improved gradually and reached nearly to equilibrium after 20 min. The short time needed for adsorption to reach equilibrium could be attributed to the high adsorption efficiency of Lewatites S-100 resin and readily available adsorbing sites (surfaces functional groups) on the adsorbent surface [16].

3.4. Effect of initial metal ion concentration at different temperature

The effect of initial concentration at different levels ranging from (40-300 mg/L) and different temperature can be seen in Fig. (4)   while keeping all other parameters constant. In Fig. [4], it is found that the removal efficiency of Co(II) was increased with enhancing sorbent/ sorbate ratio, especially at short time, but the absolute amount of Co(II) adsorbed per unit weight of Lewatite S-100   was decreased. The equilibrium times are found to be the same for all different concentration studied. Similar results are also reported by researchers for a variety of adsorbate – adsorbent systems [13,16]. The working capacity of an ion-exchanger depends on metal concentration and temperature. The surface energy of Lewatit S-100 resin decreases with temperature[21] .Similar results obtained with the sorption studies complete with the Amberlite IR-120 [21] .

3.5.Kinetic study

In the order to investigate the mechanism of adsorption, kinetic models are generally used to test the experimental data namely. Pseudo-first, pseudo-second order and Weber-Morris intraparticle

diffusion models equations can be used assuming that the measured concentrations are equals to the surface concentrations.

3.5.1. Pseudo-first order model

The Lagergren's rate equation [4] is one of the most widely used rate equations to described of an adsorbate from the liquid phase. The linear form of pseudo-first order equation is given as

$$\log\ (q_e - q_t) = \log q_e - \frac{k_f}{2.303} \qquad (4)$$

Where q_e and q_t (mg/g) are the amount of Co(II) adsorbed at equilibrium and at time t, respectively and k_f is the pseudo-first order rate constant. Fig. [5] shows a plot of log (q_e-q_t) versus t, from the slop and intercept were used to determine (k_f), complied in Table [2]. Further the correlation Coefficient (R^2=0.97) is less than 0.99 suggesting that the present adsorption system does not follow psendo-first order process.   sorption uptake, is extrapolated from the experimental data at time t = ∞ [25] .

3.5.2. The pseudo-second order model

The pseudo-second order rate model is based on the assumption that chemical sorption is the rate-limiting step, involving valence forces through sharing or exchange of electrons between sorbent and sorbate [25].

$$\frac{t}{q_t} = \frac{1}{K_{s.ads}\, q_e^2} + \frac{t}{q_e} \qquad (5)$$

Where q_e and q_t are the amount of Co(II) adsorbed (mg/g) at equilibrium and at time t, respectively, and k_s is the rate constant of pseudo-second order kinetics. The equation constants can be determined by plotting t/q_t against t. were drawn and are shown in Fig. [6].

The values of different parameters determined from the pseudo-first and pseudo-second order kinetic model along with their corresponding correlation coefficients (R^2=0.99) are presented in Table (2). This finding suggests that the present adsorption of Co(II) system can be described more favorably by pseudo-second order process kinetic model.

3.5.3 Weber and Morris intraparticle diffusion model

Kinetic data was further analysed using intraparticle diffusion model based on the theory proposed by Weber and Moirrus [26]. The amount of Co(II) adsorbed (q_t) at time (t) was plotted against the square root of time ($t^{\frac{1}{2}}$) according to Eq. [6] and the resulting plot is shown in Fig. [7].

$$q_t = k_{id} t^{\frac{1}{2}} + C \qquad (6)$$

Where k_{id} is the intraparticle diffusion rate constant and C is the intercept related to the thickness of the boundary layer according to Eq. [6], a plot of q_t

versus t$^{\frac{1}{2}}$ exhibit multi linear plots, then the process is governed by two or more steps. It is clear from Fig. [7] that the first linear portion phase (I) can be attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface. Phase (II) may be attributed to very slow diffusion of the adsorbate the surface site into the inner pores. Thus initial of portion of Co(II) adsorption by adsorbent may be governed by the initial intraparticle transport of Co(II) controlled by surface diffusion process and the later part controlled by pore diffusion. Further, such deviation of the straight lines from the origin reveals that the pore diffusion is not the sole rate controlling step [27].

3.6. Adsorptoin isotherms

The equilibrium removal of Co(II) ions investigated can be mathematically expressed in terms of the adsorption isotherms.

The Langmuir and Freundlich models are the most common isotherms used to determine adsorption phenomena. Equilibrium data obtained for Co(II) adsorption on resin were applied to Langmuir and Freundlich equations. The Langmuir models assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions [28]. The model can be represented in linear forms:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad (7)$$

Where C_e is the equilibrium concentration(mg/L), q_e the amount adsorbed at equilibrium (mg/g), Q_o and b, the Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plots of C_e/q_e versus C_e shows straight lines in Fig. (8). The Langmuir constants b and Q_o were calculated from slop and intercept, and their values are given in Table [3].

On the other hand, the Freundlich model assumes that uptake or adsorption of metal ions occurs on a heterogenous surface by monolayer adsorption. The model is described by the following equation [20].

$$\text{Log } q_e = \log K_f + \frac{1}{n} \log C \qquad (8)$$

Where q_e is the amount of adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L) and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The plots of log q_e against log C_e in as shown in Fig. (9) for various initial concentration is found to be linear indicating the applicability of the classical adsorption isotherm to the adsorbate – adsorbent system. The Frendlish parameters are also given in Table [3].

Higher values of n lie between 0 to 10

indicting favourable adsorption [20]

3.7. Thermodynamic parameters

The standard enthalpy (ΔH°) and entropy changes (ΔS°) for metal ion removal can be estimated by using the well-known thermodynamic equation.

$$\text{Log b} = \frac{\Delta S}{2.303\ R} - \frac{\Delta H}{2.303\ R}\left(\frac{1}{T}\right) \qquad (9)$$

Where b is the binding energy constant (L/g) T is the absolute temperature in kelvin (K), R is the universal gas constant (8.314) mol^{-1} K^{-1}. The standard free energy change (ΔG°) of the process can be calculated by the equation.

$$\Delta G° = -2.303\ RT\ \log b \qquad (10)$$

The plots of log b versus 1/T as shown in Fig. (10)

According to Eq. [9] yields a straight line from which enthalpy change (ΔH°) and entropy change (ΔS°) were calculate from the slope and intercept. The thermodynamic results are shown in Table [4]. Since negative value of ΔH° value obtained in this study it would be claimed that physical adsorption reactions are normally and exothermic process [29]. The negative (ΔG°) value indicates a spontaneous process. A positive (ΔS°) value indicates the affinity of the adsorbent for Co(II). [30].

3.8 The competitive adsorption of Co(II) ions from binary and ternary metal solutions:

Adsorption of coexisting multi-metal ions onto Lewatite S-100 cation exchange resin was examined. Initially effects of the presence of Ni(II) and Cr(III) on the adsorption of Co(II) were investigated in terms of equilibrium isotherm. Comparison of the adsorbed quantity of single metal ions per unit weight of Lewatite S-100 at equilibrium with the present of increasing concentration of another metal ions was given in Fig. [11] and Table [5].

The results indicate that the equilibrium uptake of single ions decreased with increasing concentration of another ion. A fixed quantity of lewatite S-100 could only offer a finite number.

From Table [5] the adsorption capacity of the ternary system will decrease in sorption in target metal solution then that of single metal ion may be ascribed to less availability of binding sites. In case of multimetal solution the binding sites are competitively divided among the various metal.

It is generally complicated to find a common rule to identify how metal properties affect the sorption. Among various factors that affect the sorption preferences of a sorbent, binding of metal ions on sorbent largely depends on physical chemical properties of metals, atomic weight, electronegativity, and ionic size will be affected for sorption [31-33] as shown in Table [4] for Co(II), Ni(II) and Cr(III).
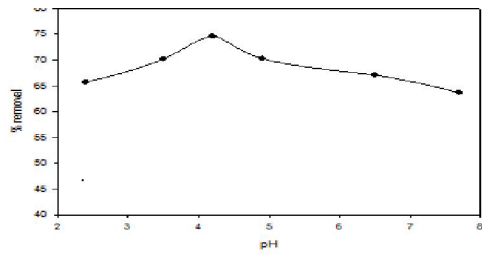
Fig.(1) Effect of the pH's on the %removal of Co(II) ion on Lewatit S-100 cationic exchange resin.
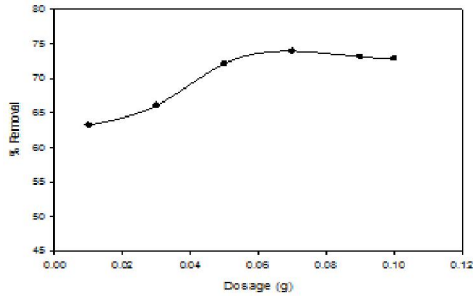

Fig: (2) Effect of the resin dosage on the % removal of Co (II) metal ion on Lewatit S-100 cationic exchange resin.
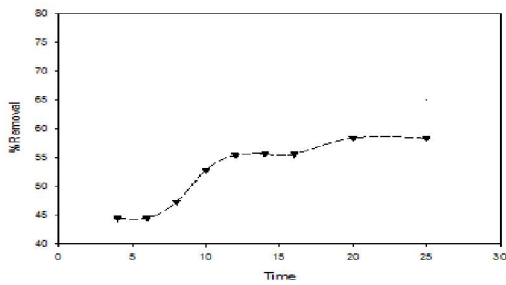

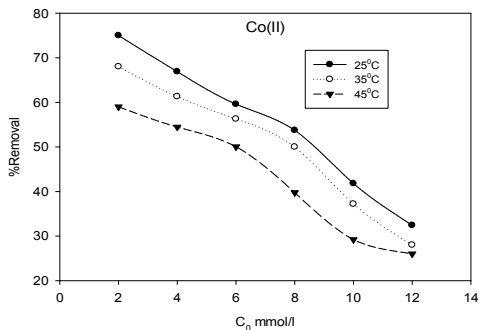**Fig: (3): Effect of agitation time on % removal of Co (II) ion on Lewatit S-100 cationic exchange resin**

Fig (4): Effect of initial metal ion concentration on % removal on Co (II) ions on Lewatit S-100 cationic exchange resin at different temperatures.
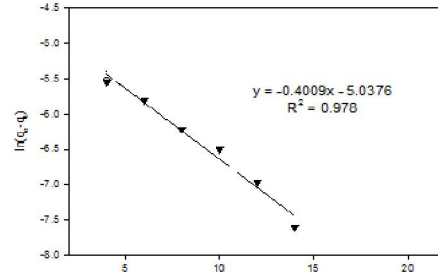

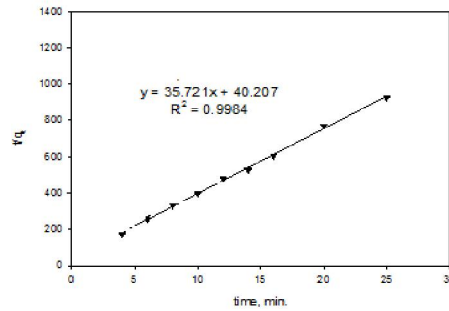**Fig.(5) Pseudo-first order of Co(II) on Lewatit S-100 at 25°C±1 and pH 4.5±0.5.**

Fig (6) Pseudo second-order for Co (II) on Lewatit S-100 cationic exchange resin at 25°C±1 and pH 4.5±0.5
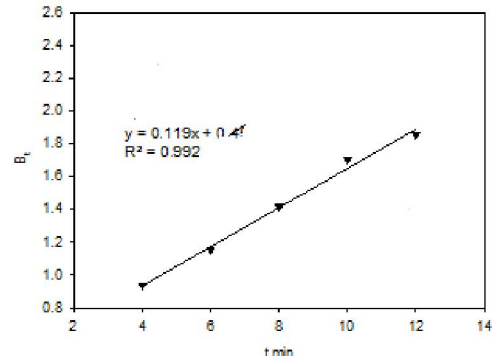

Fig (7): Particle diffusion plots of Co (II) on Lewatit S-100 cationic exchange resin at time intervals.
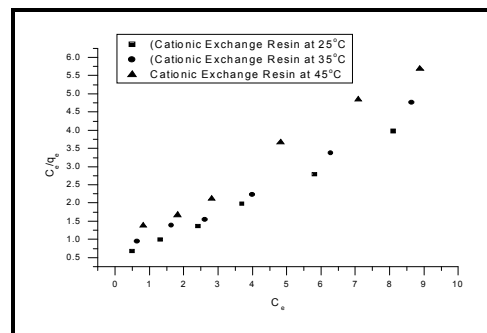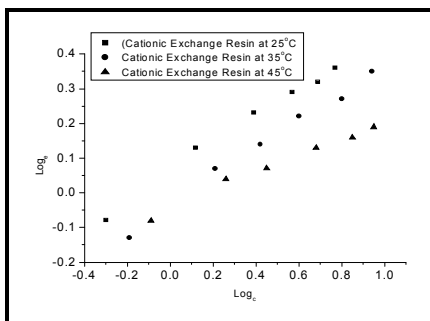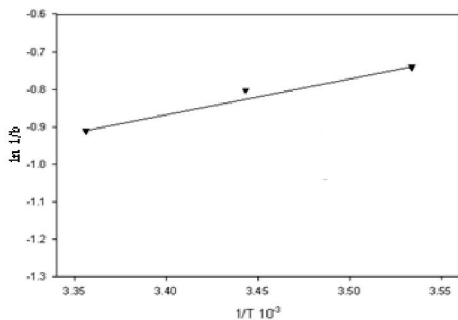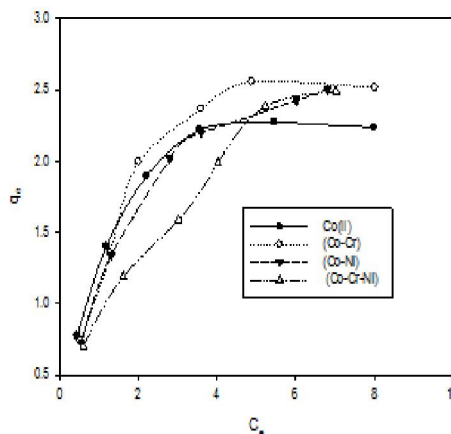

Fig: (8): Langmuir isotherms of Co(II) ions on Lewatit S-100 cationic exchange resin at 25°C, 35°C and 45°C

Fig (9): Freundlich isotherm of Co (II) ions adsorbed on Lewatit S-100 cationic exchange resin at 25°C, 35°C and 45°C.

Fig (10): Thermodynamic plotting of Co (II) on Lewatit S-100 action exchange resin.

Fig (11) Equilibrium isotherm of Co (II) ions per unit weight of Lewatit S-100 as the single metal, binary and ternary solution

Table (1). Physical and chemical properties of the resin

General Description	
Functional group	Sulfonic acid
Ionic form as, as shipped	Na^+
Structure	Gel type beads
Matrix	Cross linked polystyrene
Appearance	Brown, translucent
Physical and Chemical properties:	

Physical and Chemical properties:		
Volume change	Na+-> H max. %	8
Stabily	at pH-range	0-14
Density	Approx. g/ml	1.28
Storability Of the product	min. years	2
Storabiliy	At temperature °C	-10-+40
Total Capacity	Min .eq/l	2.0

Table (2): rate constants for pseudo- first and second order for Co (II) removal on Lewatit S-100 cationic exchange resin at 25°C

Metal	Pseudo first order		Pseudo second order	
	K_1	R^2	K_2	R^2
Co(II)	0.923	0.978	35.721	0.998

Table (3): Isotherm parameters calculated for Co (II) removal on Lewatit S-100 cationic exchange resin at 25°C

Temp.	Langmuir isotherm			Freundlich isotherm		
	V_m	K_L	R^2	K_f	n	R^2
25°C	2.478	1.110	0.996	1.138	2.443	0.992
35°C	2.099	0.981	0.987	0.917	2.413	0.991
45°C	1.769	0.743	0.997	0.896	3.862	0.988

Table (4): Thermodynamic parameters of Co(II) on Lewatit S-100 cation resin at different temperatures.

Parameters Temperature	Co(II)		
	$-\Delta G^+$	$-\Delta S^+$	$-\Delta H^+$
2598°C	22169.57	81.87	
308°C	1891.74	13.37	2226.66
318°C	1504.46	2.27	

Table (5)Comparison of the adsorbed quantity of Co(II) ions per unit weight of Lewatit S-100 at equilibrium between the solutions with Co (II) ions present as the single metal and with the presence of increasing concentration Of Ni (II) and Cr (III) ions.

C_o	Co(II)		Co-Cr		Co-Ni		Co-Cr-Ni	
	C_e	q_e	C_e	q_e	C_e	q_e	C_e	q_e
2	0.45	0.78	0.52	0.74	0.56	0.72	0.60	0.70
4	1.19	1.41	1.29	1.35	1.32	1.34	1.62	1.19
6	2.21	1.90	2.01	1.20	2.80	2.02	3.02	1.59
8	3.56	2.22	3.60	2.37	3.60	2.20	4.03	1.99
10	5.45	2.28	4.88	2.56	6.02	2.43	5.22	2.39
12	7.99	2.24	8.02	2.52	6.80	2.50	7.02	2.49

4. Conclusions

The aim of this work was to find that the Lewatite S-100 cation exchange has high exchange capacity towards Co(II) ions in the acidic medium. Batch kinetics studies showed that a rapid uptake occurred within the first 20 min and the meal uptake slowly reaches equilibrium (at 60 min). The kinetics of Co(II) sorption by Lewatite S-100 was ideally conformed to pseudo-second equation, indicating several mechanisms are involved in the adsorption process. Equilibrium sorption isotherm studies showed that the Langmuir and Frendlich isotherm model satisfactorily described the sorption data. The thermodynamic parameters illustrate that the process is exothermic and spontaneous adsorption.

The increase in negative values of (ΔG°) with increasing temperature shows that sorption of Co(II) becomes more spontaneous at higher temperatures. The presence of Co-ions such as Ni(II) and Cr(III) had appreciable inhibiting effects on Co(II) uptake by Lewatite S-100 because Ni(II) and Cr(II) had higher affinity for Lewatite S-100 surface than Co(III). Adsorptive competition was shown to reduce metal adsorption capacity in all cases. Therefore, it is essential to fully understand the mechanism of competitive adsorption of coexisting metals onto the resin for effective operation of ion-exchange process.

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