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Adsorption Characteristics of Co(II) Onto Ion Exchange Resins 1500H, 1300H and IRC 86: Isotherms and Kinetics

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Abstract: ***The uptake of cobalt from aqueous solution by Amberjet 1500H an ion exchange resin shows a remarkable increase in sorption capacity for cobalt, compared to bothAmberjet 1300H and Amberlit IRC 86 ion exchange resins. All the studies were conducted by a batch method to determine equilibrium and kinetic studies. The experimental isotherm data were analysed using bothFreundlich and Langmuir equations. The intraparticle diffusion rate constants in different temperatures were evaluated and discussed. Kinetic studies showed that the adsorption followed a pseudo-first or pseudo-second-order reaction.Thermodynamic studies revealthe feasible, spontaneous and endothermic nature of sorption processes. In addition to physical or chemical sorption processes according to nature of the resin used.***

Keywords: Cobalt; Resin; Isotherms; Kinetics and Thermodynamics

1. Introduction

The problem of removing pollutants from water and wastewater is an important process and is becoming more important with the increasing of industrial activities. In order to solve heavy metal pollution in ecosystem, it is important to bring applicable solutions to the subject. It is possible to clean polluted environment only with long study requiring expensive and complex plants. Therefore, it is important to take effective precautions to prevent water, soil and air pollutions. The cobalt containing compound is widely used in many industrial fields such as mining, metallurgical, paints, pigments and electronics. The smallest amount of cobalt is essential for human health. But its high dose may cause paralysis, diarrhoea, low blood pressure, lung irritations and bone defects [1]. Therefore, the removal of Co(II) ions from aqueous solutions, either for pollution control or for raw material recovery, has been taking on increasing importance. Therefore, it is essential that potable waters be given some treatment to remove copper before domestic supply. There are many different methods for treating wastewaters. Current methods for wastewater treatment includechemical precipitation [2], membrane filtration [3],adsorption [4], and ion exchange processes [5] and others.

2. Materials and Methods

1) Adsorbate

All the chemicals used were of analytical grade and were obtained from Aldrich, USA. A stock solution of cobalt ions was prepared by dissolving appropriate amount of $CoCl_2 \cdot 2H_2O$ in double distilled water.

2) Adsorbent

Strongcation exchange resins(Amberjet 1500H and 1300H) and weak cation exchange resin (AmberliteIRC86) from Rohm and Haas Co., used in this study without any purification.

3) Batch adsorption studies

The stock solution was diluted as required to obtain standard solutions containing 5.98mmol/l of Co(II). A 50 ml of Co(II) solution of a desired concentration, was taken in reaction bottles of 100 ml capacity and known amounts of ion exchange resins were added. The solutions were agitated for a predetermined period at the desired temperature in a shaking incubator. The concentrations of Co(II) in solution were determined before and after soaking.

The percentage of metal removal was calculated using the formula:

$$\text{Removal yield}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

Where $C_o$and $C_e$are the initial and final concentrations of the ions in the test solution, respectively, while the adsorption capacity (mmol/g) was calculated according

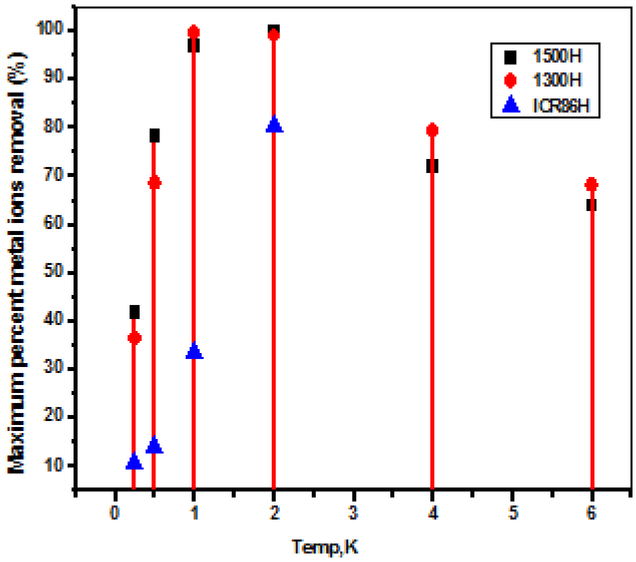
$q_t = (C_o\text{-}C_t)V/1000xW$

where V is the volume of solution and W represents the weight of the adsorbent used.

3. Results and Discussions

3.1 Effect of resin dosage on adsorption

The data clearly show that the Amberjet 1500Hresin has a high level of performance in terms of the removal of cobalt than that of Amberjet 1300H resin. Whereas the Amberlite IRC 86 resin showsa considerably lower level of performance in terms of the removal of cobalt under experimental. The observed differences may be due to the difference in the ion exchange capacity of the resins[6].



Fig,1. Effect of resin dosage on removal of cobalt ions

It may be concluded that by increasing the adsorbent dose the removal efficiency increases but adsorption density decreases. The decrease in adsorption density can be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process; whereas the number of available adsorption sites increases by an increase in adsorbent and this results in an increase in removal efficiency [7].

3.2 Influence of acidity on the sorption of cobalt

Fig. 2 shows the influence of acidity onthe sorption of the three resins for precious cobaltions. The sorption amountof both Amberjet 1500H and Amberjet 1300H resins showed the same tendency over the acidity range from 0.001 to 1.0 Mol/L HCl. The Amberjet 1500H exhibited stronger sorption ability than the Amberjet 1300H.In acidic media. Co^{2+}ions in pure aqueous medium were cationic ions.

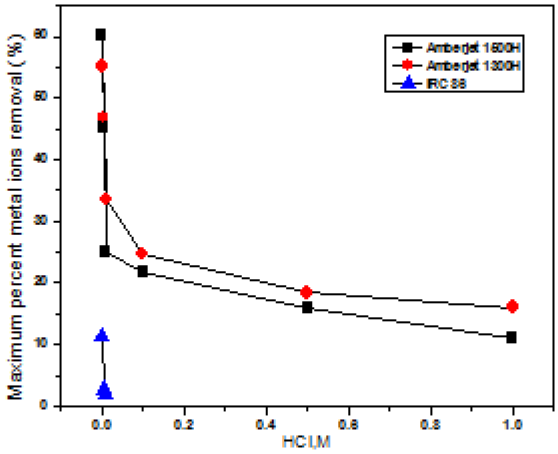


Fig.2. Effect of solution acidity on the cobalt removal by the resins

However, in acidic media, in the presence of chloride ion, it easily forms chloro-complexes in the presence of HCl(0.001 to 1.0Mol/LHCl)as a result Co^{2+}were coordinated with chloride ions and then converted into an anionic ions and $CoCl^{-}$ and $CoCl^{2-}$ complexes are the predominant species.Therefore, the sorptioncapacity for Co(II) ions gradually decreasedwith the increase of solution acidity. At higher solution acidity, carboxylic groups are present in protonated form and the active sites of the adsorbent are less available for Co(II) due to greater repulsive forces [8].

3.3 Effect of initial metal ion concentration in sorption process.

Experimental results concerning the effect of five different concentrations (2.06, 3.94, 5.98, 8.08 and 9.88 mmol/l) were presented in Fig. 3. On reviewing the data, we find out that an increase in initial cobalt ion concentration leads toincrease cobalt uptake by both Amberjet 1500H and Amberjet 1300H resin and as well asremoval percentage values (%).This is attributed to the greater the driving force through a higher concentration gradient at a high metal ion concentration [9].

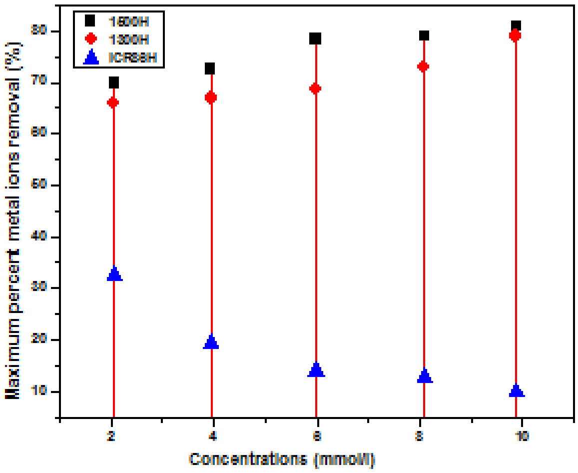


Fig.3. Effect of initial concentrations on removal of cobalt ions

On the other hand, the amount of cobalt ion uptake by Amberlite IRC 86increases (q_e,mmol/g) with increasing the initial cobalt ion concentrationup to 8.08 mmol/l then an abrupt decrease of adsorption capacity was observed when cobalt concentration increase. The low uptake was due to the surface saturation of the sorbent with metal ions [10]. In other word, as the concentration of metal ions increases, there was an increase in positive charge species in solution phase, which give rise to coulombic repulsion and results in a decrease in sorption percentage.

3.4 Effect of System Temperature

The results from Fig.4reveal that an increase in temperature results in an increase in cobalt ion uptake by the three cation exchange resins According to Wang et al. [11] the increase in sorption percentage may be due to the acceleration of some originally slow sorption steps or due to the retardation of the processes such as the association of ions, aggregation of molecules, ion pairing and complex formation in the system because of thermal agitation.

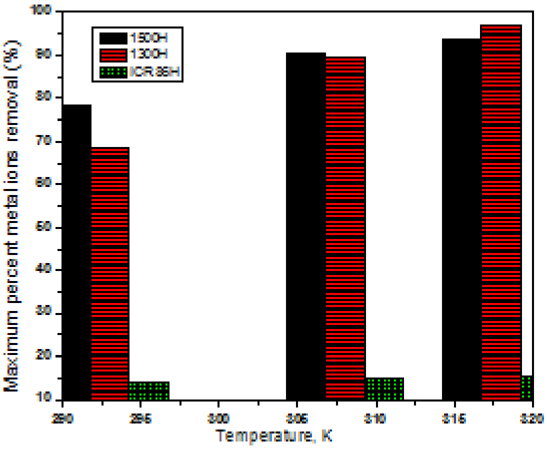


Fig.4. Effect of solution temperatures on the cobalt removal

3.5 Adsorption Isotherm Studies

Equations that are often used to describe the experimental isotherms data were Freundlich and Langmuir isotherms.The linear form of Freundlich isotherm model;

$\ln q_e = \ln K_F + n \ln C_e$
where K_F (mmol/g) is the Freundlich constant and 'n' the Freundlich exponent. Where, C_e is the equilibrium concentration (mg/L), q_e the amount of Co(II) adsorbed by per gram of the ion exchange resins and K_F and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity.

Linear plots of ln q_e versus ln C_e shows that the adsorption follows Freundlich isotherm model [12]-[13] for ICR 86 than that of Langmuir isotherm [14]-[15].K_F and n were calculated from the intercept and slope of the plot. The values of n lie between 1 and 10 indicating favourable adsorption.

The following Langmuir adsorption isotherm equation was used:
$C_e/q_e = 1/K_L Q_{max} + C_e/Q_{max}$

whereQ_{max} is the monolayer adsorption capacity (mmol/g) and (k_L) is the Langmuir constant (L/mg) related to the free energy of adsorption. The linearity of plots revealed that the adsorption followed the Langmuir isotherm model for both 1500H and 1300H resins

Table 1: Isotherm parameters.

Isotherms	Name of the resins		
	1500H	1300H	ICR 86
Freundlich			
K_F (mmol g^{-1})	0.4895	0.4667	0.11×10^4
N	6.664	6.876	0.1721
R^2	0.9540	0.7769	0.9996
Langmuir			
Q_{max} (mmol g^{-1})	0.4340	0.3906	0.0129
K_L	10.21	9.40	0.2298
R_L	0.017	0.018	2.6740
R^2	0.9982	0.9912	0.9989

Adsorption kinetics
In this study, pseudo-first and -second-order kinetic models were investigated to find the best fitted model for the experimental data. The rate linear form of Lagergren[16].

$$\ln(q_e - q_t) = \ln q_{e1} - k_1 t$$

From Table 2, it was observed that the correlation coefficient for both 1500H and 1300H systems, indicates the applicability of this model more than pseudo-second order [17]-[18] for the adsorption process and confirms the physisorptions of Co(II) onto ion exchange resin (The Figs. are not shown).

Table 2: Kinetic parameters.

Parameters	Cation exchange resins		
	1500H	1300H	IRC 86
Lagergren			
$q_{e,1}$(mmol/g)	0.4147	0.3468	0.0503
k_1 (1/min)	0.0115	0.0172	0.0133
R^2	0.9884	0.9988	0.9822
Second order			
$q_{e,2}$ (mmol/g)	0.5450	0.4619	0.0882
k_2 (g/mmol min)	0.0350	0.0683	0.6304
R^2	0.9643	0.9942	0.9959

The pseudo-second order model can be expressed as:
$(t/q_t) = (1/k_2 q_e^2) + (1/q_e)\, t$

Where (k_2) (g/mmol min) is the rate constant of the pseudo-second-order equation, q_e (mg/g) is the maximum adsorption capacity and (q_t) (mmol/g) is the amount of adsorption at time t (min). The plot of (t/q_t) vs. (t) shows a linear relationship (The Figs are not shown) . The value of qe (mmol/g) and k_2 (g/mmol min) are determined from the slope and intercept of the plot.From Table 2, it was observed that the correlation coefficients ,indicates the applicability of this model more than pseudo-first order [17]-[18]for the adsorption process and confirms the physisorptions of Co(II) onto ICR68H resin.

The intraparticle diffusion model was also applied to estimate the diffusion of Co in the resin using Weber–Morris intraparticle diffusion model [19]-[20]
$q_t = k_{int}\, t^{0.5} + C$

where q_t is the amount adsorbed (mg/g) at time t ($min^{0.5}$). Plots of q versus $t^{0.5}$(The Figs. are not shown) for different resins at different temperatures. All the plots have the same general features in that the initial curved portion followed by the linear portion to the intraparticle diffusion and the plateau to the equilibrium. K_{int} values were obtained from the slope of the linear portion of the curves for each temperature of metal ion solution. The obtained values indicated thatadsorption of the cobalt ion onto the three resins were controlled through both boundary layer effect and intraparticle diffusion rate.

3.6 Thermodynamic Parameters

The calculated Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) values for the sorption process of Co(II) by the three resins are summarized in Table 3. These values of ΔH and ΔS were obtained from the slope and intercept of the plot of ln K_D vs. 1/T (Figs. are not shown). Theobtained negative ΔG values reveal the thermodynamically feasible and spontaneous sorption process. Furthermore, the ΔG values become more and more negative with increase in reaction temperature. These results represent that the highly feasible and spontaneous sorption process can be obtained at higher temperature. The positive values of ΔH and increase in sorption percentage with rise in temperature reveal the process to be endothermic, and low magnitude of these values indicates the physicosorption nature. The positive values of ΔS reflect the affinity of the resins toward cobalt ions and also indicate that the randomness is increased at the solid/solution interface during the metal ion sorption. If we compare the ΔG values of the Co(II) sorption on Amberjet 1500H , Amberlite IRC 86 and Amberjet 1300H resins, then it can be concluded that in the latter system the ΔG values are more negative, which indicate that Co(II) Amberjet 1300H system are more feasible and spontaneous in comparison to both Amberjet 1500H and Amberlite IRC 86 resins [21].

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of the activation energy (*Ea*) and sticking probability (*S**) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage as expressed in equations:

$$\theta = 1 - \frac{Ce}{C0}$$

$$S^* = (1 - \theta)\exp\left(-\frac{Ea}{RT}\right)$$

The sticking probability, *S**, is a function of the adsorbate/adsorbent system under consideration and is dependent on the temperature of the system. The parameter *S** indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely. It can be expressed as in Table 3.

The effect of temperature on the sticking probability was evaluated throughout the temperature range from 293 to 318K by calculating the surface coverage at the various temperatures. Table 3 also indicated that the values of $S^* \leq 1$, hence the sticking probability of the Co(II) ion onto the resins systems are very high.The apparent activation energy (*Ea*) and the sticking probability (*S**) are estimated from the plot. The positive values of the apparent activation energy Ea also indicated that the higher solution temperature favours the adsorption process and also the adsorption process is endothermic in nature [22].

Table 3: Thermodynamic parameters.

Parameters	Cation exchange resins		
	1500H	1300H	IRC 86
ΔH KJ/Mol	44.05	81.86	3.312
ΔS J/Mol	142.0	266.0	22.90
Ea KJ/Mol	33.38	70.875	0.486
S*	3.15×10^{-8}	7.98×10^{-14}	0.704
ΔG KJ/Mol			
293K	-2.489	-3.710	-10.02
308K	-0.183	-0.464	-10.36
318K	-1.025	-3.093	-10.60

4. Conclusion

The work evaluates both strongcation exchange resins (Amberjet 1300H and 1300H containing sulfonated functional groups) and weak cation exchange resin (Amberlite IRC86 containing carboxylic functional groups)for removing target pollutant Co(II) from aqueous solutions and focus on the binding equilibrium and batch studies of metal ions. The adsorption degrees for the Co(II) ions were determined at different temperatures by using the three resins. Based on the efficient removal of cobalt ion from aqueous waste at 293K and 5.98 mmol/lon 1500His larger than that of 1300H due to the intrinsic ion exchange capacity, while the adsorbate/adsorbate interaction of 1500H is smaller than that of 1300H. While the adsorption capacities of Amberlite IRC86 are very weak compared to the above resins.The adsorption followed Freundlich isotherm model and pseudo second-order kinetic model. The negative ΔG and positive ΔH ensured the spontaneity and the endothermic nature of the adsorption process. The good adsorption and desorption efficiencies implied the efficacy of the resins in removing Co(II) ions from aqueous solution at low concentrations. Also, we conclude that ion exchange resins could be exploited for applications in the tertiary level treatment of potablewaters, industrial effluents as well as it can be applied for the treatment of coolant water in the nuclear power plants. Detailed studies will be needed to further evaluate ion exchange resins in the treatment of coolant water in the nuclear power plant.

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