

Adsorption Dynamics of Cobalt ion by a Novel Cation Exchanger Zirconium bismuth iodate

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ABSTRACT:

Ion exchange has a great potential to remove heavy metals from industrial wastewaters or heavy metal-containing sludge. In order to design and operate heavy metal removal processes, a new bimetallic inorganic cation exchanger Zirconium bismuth iodate (ZBI), has been synthesized by co-precipitation method and the physicochemical properties of the material were investigated to explore the adsorption process. The effectiveness of the exchanger in adsorbing cobalt ion from aqueous solution has been studied as a function of agitation time, adsorbent dosage, initial metal ion concentration, temperature, pH, and desorption. Adsorption equilibrium studies were carried out in order to optimize the experimental conditions. The kinetic experimental data fitted the Pseudo-second-order equation very well. Kinetic parameters (Gibb's free energy, entropy and enthalpy) have been evaluated. Adsorption data were modeled using both Langmuir and Freundlich adsorption isotherms. The equilibrium time was found to be 50 min for all initial concentrations studied. Desorption studies were performed with deionized water and show that ion exchange is the predominant mechanism for cobalt ion adsorption. The adsorbent was found to be both effective and economically viable.

Keywords: Zirconium bismuth iodate, bimetallic inorganic cation exchanger, kinetics and thermodynamics of ion exchange, adsorption isotherms.

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INTRODUCTION

Rapid industrialization and urbanization has resulted in the deterioration of water, air, and land quality. Natural waters are contaminated with various heavy metals arising from mining wastes and industrial discharges. The tremendous increase in the use of heavy metals over the past few decades has resulted in an increased flux of metallic substances into the environment. The heavy metals are of special concern because they are non-degradable and therefore persistent. Commonly encountered metals of concern include Pb^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} etc. These metals are toxic both in their chemically combined forms and in the elemental form.¹⁻⁴ Heavy metal contamination exists in the aqueous waste streams of many industries, such as metal plating facilities, mining operations, nuclear power plant and tanneries⁵. The soils surrounding many military bases are also contaminated and pose a risk of ground water and surface water contamination due to the heavy metals.⁶ The presence of metals in aquatic

environment is of great concern due to their toxicity to many life forms.⁷ Cobalt, a natural element present in certain ores of the earth's crust, is essential to life in trace amounts. It exists in the form of various salts. Pure cobalt is an odorless, steely-gray, shiny, hard metal. Everyone is exposed to low levels of cobalt in air, water and food.⁸

Cobalt has both beneficial and harmful effects on health; important natural sources of Cobalt in environment are soil, dust and sea water. Cobalt and its salts are used in nuclear medicines, enamels and semiconductors, grinding wheels, painting on glass and porcelain, hygrometers and electroplating; as a form stabilizer in beer, in vitamin B₁₂ manufacture, as a drier for lacquers, varnishes and paints and as a catalyst for organic chemicals. The effects of cobalt poisoning in humans are very serious, among them are asthma like allergy, damage to the heart, causing heart failure, damage to the thyroid and liver, cobalt may cause mutation (genetic change) in living cells. Some isotopes of cobalt do emit ionizing radiations. With a better awareness of the problems associated with cobalt, research studies related to the methods of removing cobalt from waste water have drawn attention increasingly.⁹

Adsorption is one of the best conventional waste water treatment methods compared to other treatment methods such as coagulation, flocculation¹⁰, reverse osmosis, ozonation¹¹, electrochemical techniques¹² and fungal decolorisation. The extent of adsorption depends on the porosity and surface area of the adsorbent. The porous structure plays a major role in the increase of adsorption rate¹³.

The main objective of this work is to investigate equilibrium and kinetic parameters of ZBI as an adsorbent for the removal of cobalt from water effluents. The parameters that influence adsorption such as initial concentration, contact time, adsorbent dosage and pH were investigated. Also ZBI has been found to be a sensitive reagent for the determination of cobalt in pharmaceutical samples.

MATERIALS AND METHODS

Materials

Zirconium oxy chloride (Loba Chemie, India), Bismuth nitrate (E.Merck) and potassium iodate (E.Merck) were used for the synthesis of the exchangers. Cobalt nitrate solution was prepared in deionized water. All other reagents and chemicals used were of analytical grade.

Instrumentation

A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements. Chemical composition was determined by ICP-AES method using ICP-AE Spectrometer Thermo Electron IRIS Intrepid II. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies. A scanning electron microscope (JOEL JSM-5600 Digital) was used to characterize the exchanger for its morphological information.

Preparation of adsorbent

Zirconium bismuth iodate cation exchanger was prepared¹⁴ by adding 0.05M potassium iodate solution to a mixture of 0.05M zirconyl oxychloride solution and 0.05M bismuth nitrate solution with intermittent shaking of the mixture, keeping the pH at 1.0. It was then filtered, washed with deionized water and dried. The exchanger was then converted to H⁺ form by treating with 1M nitric acid for 24 hours with occasional shaking and intermittent changing of acid. It was

then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60-100 mesh.

Adsorption experiments

The adsorption experiments were carried out by agitating 200 mg of adsorbent with 20 mL of Co(II) solutions (0.005-0.04M) at 150 rpm on a shaker at 298K. The concentration of Co(II) remained in the solution, after being centrifuged was analysed by complexometric titrations. In this study, the effects of several factors such as, pH, concentration of Co(II) solution, adsorbent doses, temperature (303, 313, 323 and 333K) and contact time on Co(II) removal efficiency were examined⁹.

Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. Langmuir and Freundlich equations were used to interpret the experimental data¹⁵.

From the batch adsorption experiments, the adsorbed amount (q_e) of Co(II) per unit of sorbent mass was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \text{ ----- (1)}$$

Where C_0 is the initial cobalt concentration, C_e is the concentration of cobalt at equilibrium (mg/L), m is the mass of adsorbent (mg) and V is the solution volume (L).

Adsorption Kinetics

The sorption kinetics describe the solute uptake rate which in turn governs the residence time of a sorption reaction. It is one of the important characteristics in defining the efficiency of a sorption process. Hence, in the present study, the kinetics of cobalt removal has been carried out to understand the behavior of the adsorbent⁵. The kinetic experiments were conducted in batch mode. The experimental details were as follows: 200 mg of ZBI was added to 20 mL of 0.01M Co(II) solution. The suspension was shaken for a period 10 and 180 min with a rotary shaker at a speed of 150 rpm. After being centrifuged, Co(II) was analysed by complexometric titrations. The Co(II) concentration after adsorption at 0.5 min and at infinite time (24 hr) were also determined. All experiments were carried out in duplicate¹⁶.

The influence of pH in the range of 1-13 was studied by taking cobalt concentrations (0.01M and 0.02M), adsorbent dose 200 mg and temperature 30⁰C. The pH of Co(II) solution was adjusted after adding the adsorbent by using dilute NH₃ and HCl solutions. Also the pH of ZBI suspension was measured before and after Co(II) adsorption on ZBI surface as follows: 20 mL of Co(II) solution (0.01M) was added to ZBI. The pH is registered at the first moments of addition and after attaining equilibrium¹⁶.

The adsorption efficiency of Co(II) on ZBI was studied at different adsorbent doses (0.1-1g per 20 mL Co(II) solution) at Co(II) concentration 0.01M, keeping stirring speed 150 rpm, temperature 30⁰C and contact time 1 hr constant¹⁶.

Initial cobalt concentration ranging from 0.005M to 0.04M was prepared and adsorption experiments were conducted using 0.2g of the exchanger.

To study the effect of temperature on the adsorption of cobalt the experiments were carried out at temperatures varying from 303K to 333K with initial cobalt concentrations of 0.01M and 0.02M.

Desorption studies

Desorption studies were carried out to analyse the mechanism of adsorption and recovery of the adsorbate and adsorbent. The regeneration of the adsorbent may make the treatment process economical. The supernatant was separated after centrifugation and the adsorbent was separated and allowed to agitate with 20 mL of deionized water above the equilibrium time of adsorption. The desorbed Co(II) solution was separated by centrifugation and estimated by complexometric titrations using EDTA¹⁷.

Determination of Co(II) in pharmaceutical samples

0.5g of pharmaceutical sample was dissolved in boiling with 10 mL of aquaregia. The solution was evaporated to dryness and the residue was dissolved in 10 mL of 1M HCl filter, if required and solution was diluted to 100 mL with doubly distilled water. Then the concentration of Co(II) in the solution was analysed by complexometric titrations.

Results and Discussion

Samples of Zirconium bismuth iodate (ZBI) of various composition have been synthesized but ZBI₃ obtained as white powder having maximum ion exchange capacity, 1.32 meqg⁻¹ was selected for detailed studies (Table 1). The composition of ZBI obtained from EDS analysis was found to be Zr:Bi:I::1:1.8:2.1 (figure 1).

Table1: Synthesis and properties of various samples of exchanger using 0.05 M solutions each.

Sample	Volume ratio	pH	Appearance	Ion Exchange Capacity For Na ⁺ (meq/g)
ZBI ₁	1:1:1	1	White powder	0.95
ZBI ₂	1:1:2	1	White powder	1.02
ZBI ₃	1:1:3	1	White powder	1.32
ZBI ₄	1:2:3	1	White powder	1.10
ZBI ₅	1:2:3	1	White powder	1.19

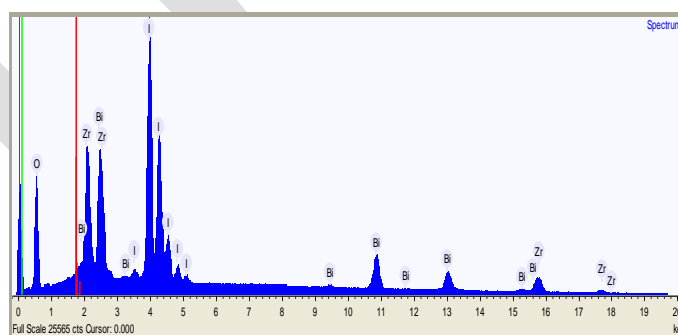


Figure 1: EDS of ZBI

FTIR spectra of ZBI (figure 2(a)) showed a broad band in the region $\sim 3444\text{ cm}^{-1}$ which is attributed to symmetric and asymmetric -OH stretching, while the band at $\sim 1622\text{ cm}^{-1}$ is attributed to H-O-H bending¹⁸. Bands at $\sim 1333\text{ cm}^{-1}$ and 1041 cm^{-1} indicates the presence of structural hydroxyl protons in ZBI. Bands at $\sim 723\text{ cm}^{-1}$ and $\sim 603\text{ cm}^{-1}$ may be due to the presence of Zr-O and Bi-O bonds. XRD analysis (Figure 2(b)) shows no characteristic peaks at

different 2θ values, indicating the amorphous nature of the exchanger. The Scanning Electron Microscope image (figure 2(c)) of ZBI explain that the particles were broad in size, having an irregular shape and no sign of crystalline structure¹⁹. The thermogram of ZBI (figure 2(d)) suffers a first weight-loss of approximately 11% up to 165°C, attributed to the loss of moisture and hydrated water²⁰. Then the sample is almost stable up to 500°C and a continuous weight loss was observed after at 500°C which is due to decomposition of the material to the corresponding oxide.

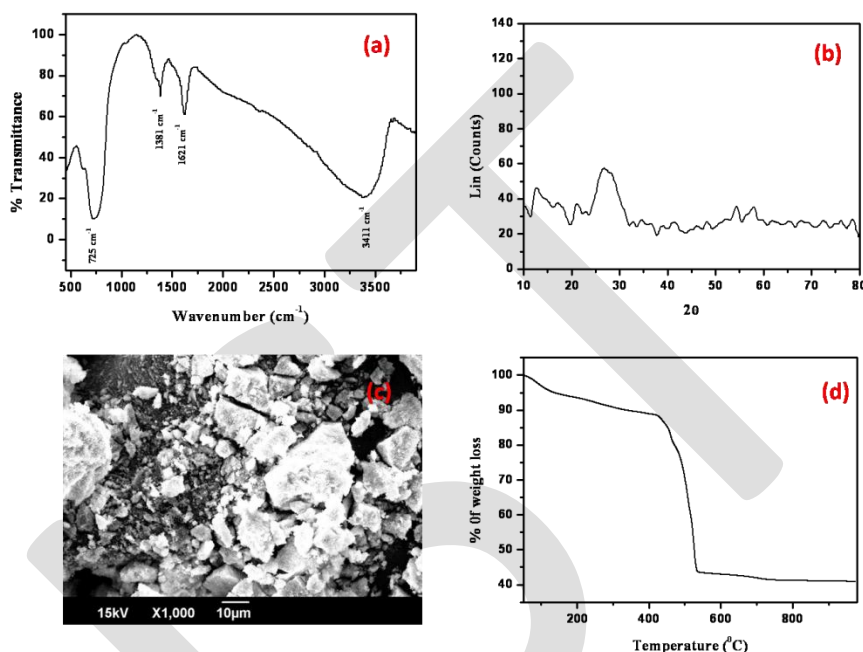


Figure 1: (a) FTIR of ZBI, (b) XRD of ZBI, (c) SEM of ZBI and (d) TGA of ZBI

Kinetic studies

Effect of contact time

Figure 3(a) shows the effect of contact time on the removal of Co(II) by ZBI exchanger. More than 80% of Co(II) adsorbs in first 50 minutes, reaching soon after equilibrium. Although the equilibrium is achieved in 60 minutes, hence a contact time of 1 hr was selected for further studies.

Lagergren first-order reaction model (eq.2) and Ho et al.'s pseudo-second-order reaction model²¹⁻²² (eq.3) were used to describe the kinetics of cobalt adsorption on ZBI. The first order Lagergren rate equation²³⁻²⁶ is in the form;

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \text{ -----(2)}$$

Where k_1 is the Lagergren rate constant for adsorption(min^{-1}), q_e is the amount of metal ion adsorbed at equilibrium(mg/g), and q_t is the amount of metal ion adsorbed at any given time t (mg/g).

Ho et al.'s²⁷ pseudo-second-order rate equation is given by:

$$\frac{1}{q_t} = \frac{1}{2Kq_e^2} + \frac{1}{q_e} \quad (3)$$

$$h = k_2 q_e^2 \quad (4)$$

Where K_2 (g/mg.min) the rate constant of pseudo-second-order adsorption, h is the initial adsorption rate (mg/g.min) and q_e and q_t are the amount of adsorbed cobalt on adsorbent (mg/g) at equilibrium and at time t , respectively.

The plot of $\ln(q_e - q_t)$ versus t (not presented here) shows a straight line with a very low correlation factor, $R(0.0260)$, indicating that the cobalt removal with ZBI is not a first-order reaction. Ho's pseudo-second-order-model described the best kinetic data (figure 3(b)) (correlation coefficient R close to 1). The rate constant K_2 , the correlation coefficients, the initial adsorption rate (h) and the removal capacities at saturation (q_e) were calculated from the values of the slopes and intercepts according Ho's pseudo-second-order model and are compared in the table 1 with the Lagergren first-order model.

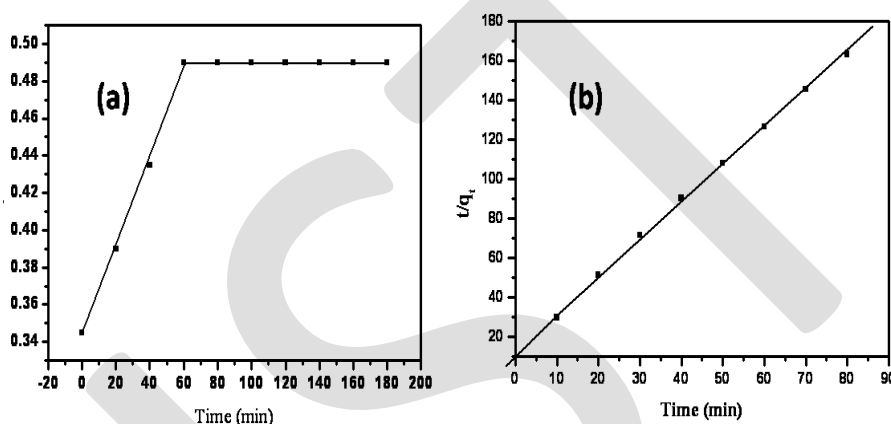


Figure 3: (a) Effect of contact time and (b) Pseudo-second-order adsorption

Table 2: Parameters for adsorption of Co(II) onto ZBI derived from the pseudo-first-order and second-order-kinetic-models

Pseudo-first-order			Pseudo-second-order			
q_e (mg/g)	K_1 (min ⁻¹)	R^2	q_e (mg/g)	K_2 (g/mg.min)	h (mg/g.min)	R^2
1.1818	0.0187	0.6771	9.1505	1.9241	161.11	0.9996

Effect of pH

Adsorption process for the treatment of Co(II) solution is pH dependent. The plots of adsorbed amount versus pH of cobalt (figure 4(a)) solution have inflection points at pH 6 where significant adsorption of cobalt actually begins. With an increase of pH of the solution from 2.0 to 5.0, the removal capacity decreases, then increases gradually till pH = 8. After that a drastic increase of cobalt adsorption occurs at an initial Co(II) concentration of 0.01M and 0.02M respectively, which was due to the precipitation of cobalt ions as insoluble $\text{Co(OH)}_{2(s)}$ precipitate rather than the adsorption on ZBI¹⁶. Hence in the present study, an optimum pH of 6.0 was selected for cobalt- ZBI system.

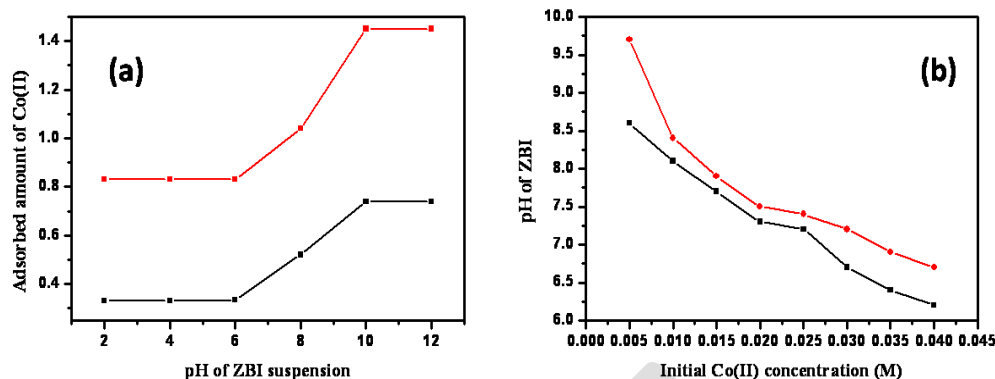


Figure 4: (a) Effect of pH on Co(II) adsorption (b) pHs of ZBI suspension before and after Co(II) adsorption

Measuring the pHs of the ZBI suspension before and after Co(II) adsorption can give good information for revealing the above comments. Figure 4(b) shows the pH values of ZBI suspension before and after Co(II) adsorption. It was observed that the pH of ZBI suspension decreases with increasing Co(II) concentration before and after Co(II) adsorption. This result is probably due to the formation of the acidic Co(II)-aqua complex¹⁹. Therefore, the larger the Co(II) concentration the higher is the solution acidity.

Effect of adsorbent dosage

Figure 5(a) shows the percentage adsorption of cobalt solution onto ZBI exchanger versus adsorbent dosage. Effective adsorption is observed while increasing the adsorbent dosage. It is evident from the figure that the percentage adsorption of cobalt increases due to the availability of more adsorption sites at higher concentrations of the adsorbent¹⁵. Maximum of 81.5% cobalt is adsorbed by 1g of ZBI.

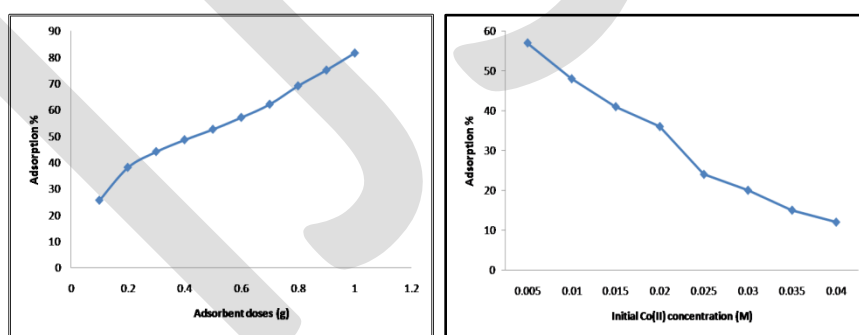


Figure 5: (a) Effect of adsorbent dosage (b) Effect of Co(II) concentration

Effect of initial cobalt(II) concentration

Figure 5(b) reveals that as the concentration of cobalt increases, the adsorption efficiency by the exchanger decreases. This is due to increase in cobalt concentration, surface area, saturated active sites of the adsorbent and hence the adsorption efficiency is decreased.

Effect of temperature

The adsorption capacity of ZBI exchanger towards cobalt is found to increase with a rise in temperature indicated that the process is endothermic. The enhancement in the adsorption

capacity might be due to the enhancement of adsorptive interaction between the active sites of adsorbent and adsorbate ions.

Adsorption isotherms

Langmuir isotherm

Langmuir isotherm theory²⁸⁻²⁹ is based on the assumption that adsorption on a homogeneous surface and is used to determine the maximum capacity of adsorbent. The linearised form of the Langmuir adsorption isotherm equation is,

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \text{----- (5)}$$

Where K_L is the Langmuir constant; q_m is the maximum adsorption capacity (mg.g^{-1}) and q_e is the adsorbed amount of Co(II) at equilibrium (mg.g^{-1}). The values of K_L and q_m were determined from experimental data by linear regression, i.e, a plot of c_e/q_e versus c_e (figure 6(a)) indicates a straight line of slope $1/q_m$ and intercept of $1/(K_L q_m)$.

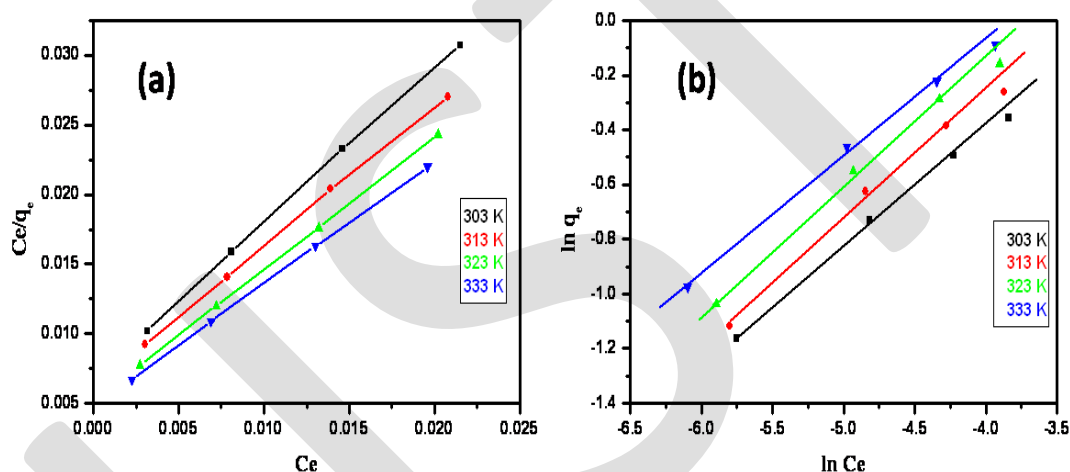


Figure 6: (a) Langmuir Isotherm models (b) Freundlich Isotherm models

Fruendlich isotherm

Freundlich isotherm is a model based on the distribution of solute between the solid phase and liquid phase at equilibrium. The Freundlich equation is expressed as follows;

$$q_e = K_F C_e^{1/n} \text{----- (6)}$$

Where, K_F and n are Freundlich constants that are related to the adsorption capacity and adsorption intensity respectively. The values of K_F and n were obtained from the linear plots of $\ln q_e$ versus $\ln C_e$ (figure 6(b)). The data in table 2 presents the results, along with associated correlation coefficient (R^2). Also the data in table 2 reveals that according to the correlation coefficients, the Langmuir model yields a better fit than the Freundlich model. Maximum monolayer adsorption of cobalt onto ZBI shows that the exchanger used in the present study has a relatively good adsorption capacity. Strong positive evidence for the good adsorption capacity is also obtained from the correlation coefficients R^2 as shown in table 2.

Table 3: Parameters for Langmuir and Freundlich Isotherm models

T (K)	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mol)	R^2	K_f	n	R^2
303	1.1601	131.68	0.9997	0.0154	2.2050	0.7257
313	0.9961	162.36	0.9996	0.0363	2.0963	0.8021
323	1.0590	185.04	0.9999	0.0466	2.0898	0.8029
333	1.1498	186.51	0.9999	0.0698	2.3444	0.8058

Thermodynamic studies

Spontaneity of a process can be determined by thermodynamic parameters such as enthalpy change (ΔH^0), free energy change (ΔG^0) and entropy change (ΔS^0). A spontaneous process will show a decrease in ΔG^0 value with increasing temperature. The thermodynamic parameters of adsorption, i.e., enthalpy change (ΔH^0), free energy change (ΔG^0) and entropy change (ΔS^0) were calculated using the following equations³⁰:

$$\Delta G^0 = -RT \ln K_L \text{ ----- (7)}$$

$$\ln K_L = \Delta S^0/R - \Delta H^0/RT \text{ ----- (8)}$$

Where R is the general gas constant ($\text{KJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), $K_L = K_{\text{ads}}/K_d$ is the Langmuir adsorption constant and T is the temperature (K). ΔH^0 and ΔS^0 values can be obtained from the slope and intercept of the Van't Hoff plots of $\ln K_L$ (from the Langmuir isotherm) versus $1/T$ ³¹⁻³². The results of these thermodynamic calculations are shown in figure 7 and table 4.

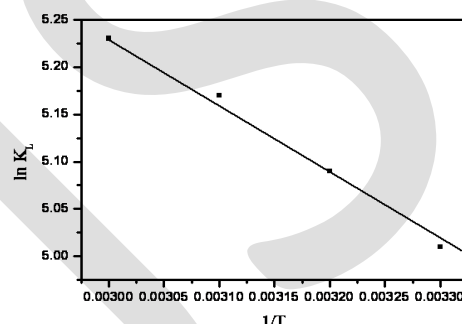


Figure 7: Plot of the Langmuir adsorption constant ($\ln K_L$) vs temperature ($1/T$)

Table 4: Thermodynamic constants for the adsorption of Co(II) on ZBI at various temperature

T (K)	$\ln K_L$	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol/K)
303	5.01	-12.62	707.13	5.25
313	5.09	-13.25		
323	5.17	-13.88		
333	5.23	-14.48		

The negative value for the Gibbs free energy for Co(II) adsorption shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The overall adsorption process is endothermic ($\Delta H = 707.13 \text{ KJmol}^{-1}$). This explains why the Co(II) adsorption capacity of ZBI increases with increasing temperature. Table 3 also shows that the ΔS value was positive, indicating that the heavy metal ions near the surface of the adsorbent is more ordered than in the subsequent adsorbed state (the

Co(II) ions exist in the aqueous phase in a very well-ordered state, namely as an aqua complex). In the other words, it is the dehydration of the cations that leads to the observed increase in entropy³³. Adsorption is thus likely to occur spontaneously at relatively normal and high temperatures because $\Delta H > 0$ and $\Delta S > 0$.

Desorption

In the desorption studies, deionized water was used as desorption agent. The exchanger samples loaded with different adsorbed amount of Co(II) ions (initial cobalt concentration ranging from 0.005M to 0.02M) were placed in 50mL deionized water at room temperature and the amount of cobalt ions desorbed within 1 hr is measured. Figure 8 shows the data of the adsorbed and desorbed amount of Co(II) ions. The data showed that there is about 33.73%, 34.07%, 31.88% and 29.12% Co(II) ions desorbed from ZBI surface loaded by 85.02%, 77.59%, 73.40% and 79.50% Co(II).

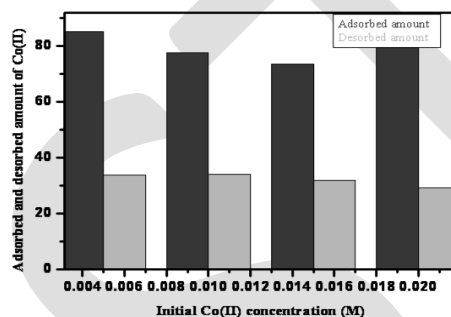


Figure 8: Adsorbed and desorbed amount of Co(II) from ZBI surfaces

Determination of Co(II) in pharmaceutical samples

The analytical importance of the exchanger can be explored by determining Co(II) in pharmaceutical samples of Becosules capsules. The results of the analysis of the samples were shown in table 4, which were comparable with those obtained by the standard method³⁴ for Co(II). Hence the exchanger ZBI is a sensitive reagent for the determination of cobalt in pharmaceutical samples.

Table 5: Determination of Co(II) in pharmaceutical samples

Samples	Co(II) found by present method(μg/%)	Co(II) found by Nitroso R-salt method(μg/%)
1. Becosules capsules 1	14.57	14.61
2. Becosules capsules 2	14.52	
3. Becosules capsules 3	14.50	

CONCLUSION

Adsorption studies indicate that the exchanger Zirconium bismuth iodate readily retains Co(II) ions. The optimum pH for Co(II) adsorption was 6.0. Kinetic studies indicated that equilibrium for cobalt adsorption on ZBI is established in less than 1 hr and the Ho et al's pseudo-second-order reaction rate model was found to describe the best kinetic data. Isotherm

analysis of the data showed that the adsorption pattern for cobalt(II) on ZBI followed the Langmuir isotherm, the adsorption process is endothermic and increased with increasing temperature. Also as the adsorbent was increased the adsorption percentage was increased.

All the above results clearly show that the exchanger Zirconium bismuth iodate can be used effectively as an adsorbent for the removal of cobalt metal ions from aqueous solution.

Acknowledgements

Author acknowledges the Council of Scientific and Industrial Research for awarding Junior Research Fellowship and STIC, Cochin, School of Chemical Sciences, M G University, Kottayam for providing technical facilities.

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