TREATMENT OF LOW– AND INTERMEDIATE– LEVEL RADIOACTIVE LIQUID WASTE FROM ALTWATHA SITE USING IRAQI ZEOLITE

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ABSRTRACT

Ion exchange material used in this study is synthetic inorganic resin. It is Iraqi synthetic zeolite type Na-A, which was prepared from Iraqi kaolinite. The prepared zeolite pellets were solidified by heat treatment at 600°C for 3 hours.

Nine radiochemical experiments were carried out on real (radioactive) samples. Five of these experiments were to study the uptake rate (sorption rate) of cobalt-60. The measured value for equilibrium time was one hour. The other experiments were carried out to obtain sorption isotherm using batch test. The product cobalt concentration was fitted to Langmuir and Freundlich isotherms as followed respectively:

$$\frac{x}{m} = 1.25\ C_e / (1+6*10^4\ C_e)$$

$$\frac{x}{m} = 8*10^{-4}\ C_e^{0.4}$$

Gamma spectrometry analysis system of Sodium Iodide (NaI) detector coupled with a multichannel analyzer, was used for the measurements of radioactivity of the samples pre- and after treatment with zeolite.

In general the experimental results have shown an efficient performance of the Iraqi zeolite to remove different cobalt concentration from low- and intermediate- level radioactive liquid waste.

خلاصة

مادة المبادل الايوني المستخدمة في هذا البحث هو نوع صناعي لا عضوي, زيولايت نوع Na-A المحضر من الكاؤلين العراقي. حبيبات الزيولات تم تصليبها بالتسخين لدرجة 600°م ولمدة ثلاث ساعات.

تسعة تجارب أجريت على نفايات سائلة مشعة مأخوذة من موقع التويثة. قسم من هذه التجارب (خمسة) لدراسة معدل الامتزاز (Sorption rate), وتبين أن الفترة الزمنية اللازمة للوصول إلى حالة التوازن هي ساعة واحدة. التجارب الباقية (أربعة) فقد أجريت لدراسة علاقة التوازن بثبوت الحرارة (Sorption Isotherm).
ووجد أن العلاقة مطابقة لمعادلتي لانكمير (Langmuir) وفرندلش (Friendliest) وحسب ما يلي:-

$$\frac{x}{m} = 1.25\ C_e / (1+6*10^4\ C_e)$$

$$\frac{x}{m} = 8*10^{-4}\ C_e^{0.4}$$

التحليل للنماذج أعلاه تم باستخدام جهاز قياس أطياف أشعة كاما المعتمد على الكاشف الوميضي أيود يد الصوديوم (NaI) المرتبط بمحلل متعدد القنوات (Multichannel Analyzer).

النتائج أظهرت كفاءة الزيولايت العراقي نوع Na-A في إزالة النظير المشع Cobalt-60 من النفايات السائلة ذات النشاط الإشعاعي الواطئ والمتوسط

KEYWORD

Zeolite**,** sorption rate, sorption isotherm, cobalt ions, distribution coefficient, total sorption capacity.

INTRODUCTION

There are many sources of low-and intermediate- level radioactive liquid waste in Altwatha site, those include radiochemical, radiomedical and reactors. All these activities were stopped after the war at 1991.

Radioactive liquid waste from all these activities are collected and stored in storage tanks of Rad Waste Treatment Station (RWTS).

14-Tammuze reactor, Material testing reactor, MTR (swimming pool reactor type), its containment building was destroyed completely and the reactor pool was opened to the surrounding environment. Emergency and health physics teams had been emptied the radioactive liquid waste from the pool and filled with other clean water in order to reduce exposure to the surrounding environment. Radioactive liquid waste used in this study, is from reactor pool. The pollutant cobalt-60 in the liquid waste came from neutron activation for corrosion products.

Radiations can produce harmful effects on living organisms. Partly as a result of ignorance and partly due to accidental circumstances, a number of cases of injury, ranging from minor early skin lesions to delayed bone cancer and leukemia, where reported among radiologists and others who were exposed to excessive amount of radiations. When the first definitive "maximum permissible" levels of exposure to radiation were instituted, their general acceptance leads to a marked decrease in incidence of radiation injuries (Samuel, 1981).

Natural Zeolites were first discovered in 1756, by the Swedish mineralogist Freiherr Cronstedt (Mumpton, 1983). However, it was not used until the late 1950s, that researchers showed their effectiveness for environmental protection and remediation (Karen, 2000).

Ebenezer, (1984) was mentioned that the use of zeolites towards decontamination of low- and intermediate- level radioactive liquid waste and as carriers of target elements in a nuclear reactor has received considerable attention.

After the resin has been exhausted in treating radioactive liquid waste, there is no regeneration and it will disposed as radioactive solid waste (Karen, 2000). The radionuclides are not destroyed but rather are removed from the waste stream and concentrated on the solid matrix (resin).

Sample of Iraqi synthetic type A zeolite as crystalline with molecular formula Na_2O:0.79, Al_2O_3:1, SiO_2:1.95, powder and pellets are prepared in Iraqi Atomic Energy Commission (IAEC) Laboratories, which was used as material under investigation in this study.

Gamma Spectrometry, NaI scintillation detector, was used to determine radioactivity concentration of samples before and after treatment using Iraqi zeolite .

Atomic Adsorption Spectrophotometry, was used to determine the total concentration of pollutant (radioactive and non radioactive cobalt).

This study is also concerned with the application of ion exchange because ion exchange is becoming more and more important in the treatment of water and wastewater. The industrial usage of ion exchange has been broadening to such classic operation as adsorption, distillation, and filtration (Kunin, 1963).

Ion exchange is a chemical treatment process used to remove unwanted ionic species from wastewater. It is basically a simple process based on reversible interchange of ions between liquid and solid (that is, the resin) with no permanent changes in the structure of the solid (ABB, 1999).Cation exchange resins contain fixed electro negative charged, which interact with mobile counter ions having the opposite (positive) charge (Considine, 1974).

The major goal of this research is to minimize the volume of radioactive liquid waste and incorporate the radionuclides into a solid matrix in order to prepare for final disposal.

EXPERIMENTAL ARRANGEMENT & PROCEDURES

Materials

Sorbent

Zeolite was used as sorbent, it was the artificial widely available and cheaply sold zeolite, type A in the sodium form (Na-A) as developed for use in detergents. This material was prepared from Iraqi Kaolinite (mixed with 2Normality sodium hydroxide at boiling point for two hour under agitation) [Al-Mashta, 1989]. The product was mixed with natural kaolinite in specific proportion as cross linking material to form pellets. These pellets were calcined in the furnace at 600°C for three hours for solidification.

Crystalline powder zeolite sorbent was used in static equilibrium experiments, Elemental analysis was accomplished in the Geological Survey and Mining Company's Laboratories, Table 1.

Table 1 : Zeolite Composition.

Element	Percentage %
SiO_2	34.48
Al_2O_3	29.94
L.O.I.	15.05
Na_2O	13.4
CaO	2.52
TiO_2	1.70
Fe_2O_3	0.95
MgO	0.08
K_2O	0.03

Sorbate

Cobalt (Radioactive and Non Radioactive) which included in:-

- Radioactive Liquid Waste from Altwatha site (Reactor Pool), which contains Co-60 from neutron activation of corrosion product.
- Simulant Solution prepared in Lab. Using Cobaltous oxide, CoO (carrier free of Co-60)

Equipment

Gamma Spectrometry, NaI Scintillation Detector:

Sodium Iodide scintillation detector was used to analyze radioactivity concentration of samples. It is coupled with a multichannel analyzer Fig.1. Scintillation detector consists of two main parts, the first is sodium iodide crystal containing small quantity of thallium, the second is photomultiplier .When a photon passes through the crystal , it will cause emitting of light in a visible band. This light when falling on photocathode will give an electrical pulse, which can amplified immediately by photomultiplier (Khalid , 1988).

The system must be calibrated using sources with known radioactivity, usually Co-60 and Cs-137 standard small solid sources are used for calibration.

Fig. (3-4): Gamma Spectrometry, NaI Scintillation Detector.

The sample placed in a special container (1 liter), sample volume must be not less than 250 milliliters. The sample must weight accurately.

The counting started after fixing the sample at the right place and closing the shielded region. For accuracy, counting time must be not less than one hour.

Atomic Adsorption Spectrophotometry

- Auxiliary equipment:

A. Oscillating shakers.
B. Centrifuge.
C. Electrical Balance.

Experimental Procedures

Static equilibrium experiments were used to study the sorption rate and sorption isotherm of cobalt-60 on synthetic type A zeolite using radiochemical measurements.

Determination of sorption rate

250 ml of radioactive liquid waste was placed into (1L) beaker. Accurately weighted amount of zeolite powder (0.5 gram) was added to five of these beakers. Each beaker was sealed with parafilm and placed in an oscillating shaker at 90 rpm Fig.2 . Each beaker was shaked for a various period of time (10, 30, 60, 120, 180) minutes.

Fig.2 :Oscillating Shaker.

After shaking, the content was distributed into six closed plastic ampoule, then placed in a centrifuge (10000 rpm) for 30 minutes.

The supernatant of all ampoules were collected into (1L) beaker, then transferred to special container to analyze in Gamma Spectrometry Scintillation Detector.

Determination of Sorption Isotherm

250 ml of radioactive liquid waste was placed into five (1L) beakers. Accurately weighted amounts of zeolite powder (0.25, 0.73, 1.02, 2.0 g) were added to these beakers and the 5th was left to serve as a blank.

Each beaker after sealing by parafilm was placed in an oscillating shaker (90 rpm) for 4.5 hour to reach equilibrium (from previous experiment it was found that one hour is sufficient for reaching equilibrium).

The content of each beaker was distributed into six closed ampoule, then placed in a centrifuge (10000 rpm) for 30 minutes. The supernatant was collected into (1L) beaker, and then transferred to special container to analyzed using Gamma Spectrometry Scintillation Detector.

RESULTS AND DISCUSSION

Source Sample Analysis*:*

Source Sample was analyzed in gamma spectrometry scintillation detector (NaI) Sodium Iodide type. The analytical graph is presented in Fig. (4-1).

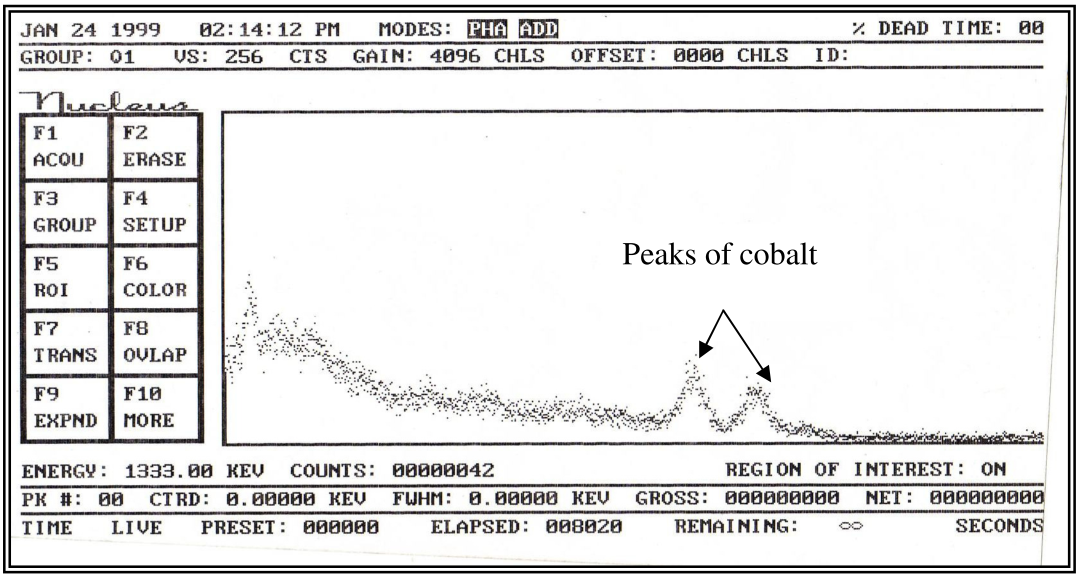

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Fig. 3: Analytical Graph of Source Sample.

Radioactivity concentration of this sample was calculated and found to be 19.684 kBq/m^3 (4.8x10^{-13} kg/m^3 radioactive cobalt). For the analyses of the results GDR computer program was used.

From Fig.3, it was observed that the radioactivity of sample comes from cobalt-60, which present in the reactor coolant by neutron activation of corrosion products, the below reaction was followed:

$$\mathbf{Co}^{59} + n \longrightarrow \mathbf{Co}^{60} + \gamma \qquad (1)$$

$$\mathbf{Co}^{59}\ (n, \gamma)\ \mathbf{Co}^{60}$$

The same sample was analyzed by Atomic Adsorption Spectrophotometry, the results show that total cobalt concentration was 0.0929 ppm (9.29x10^{-5} kg/m^3).

Batch Experiments

Sorption Rate

The radioactivities of samples after treatment with 0.5g zeolite powder at different shaking time were tabulated in Table 2.

Table 2: Radioactivity Concentrations of Different Shaking Time.

Beaker No.	Volume of sample *10^4(m^3)	Weight of zeolite, *10^3(kg)	Shaking Time (s)	Activity of Supernatant,A_f (kBq/m^3)	Distribution Coefficient,Kd_r *10^3(m^3/kg)
1	2.5	0.5	600	19.273	10.66
2	2.5	0.5	1800	17.41	65.31
3	2.5	0.5	3600	14.51	178.29

4	2.5	0.5	7200	14.291	188.68
5	2.5	0.5	10800	14.35	185.85

Radioactivity of sample (A_o) = 19.684 kBq/m^3.

Figure 4 shows the different shaking time with the radioactivity of samples.

From Fig. 4, it was observed that the time needed for the equilibrium between cobalt-60 ions and the zeolite was at least one hour.

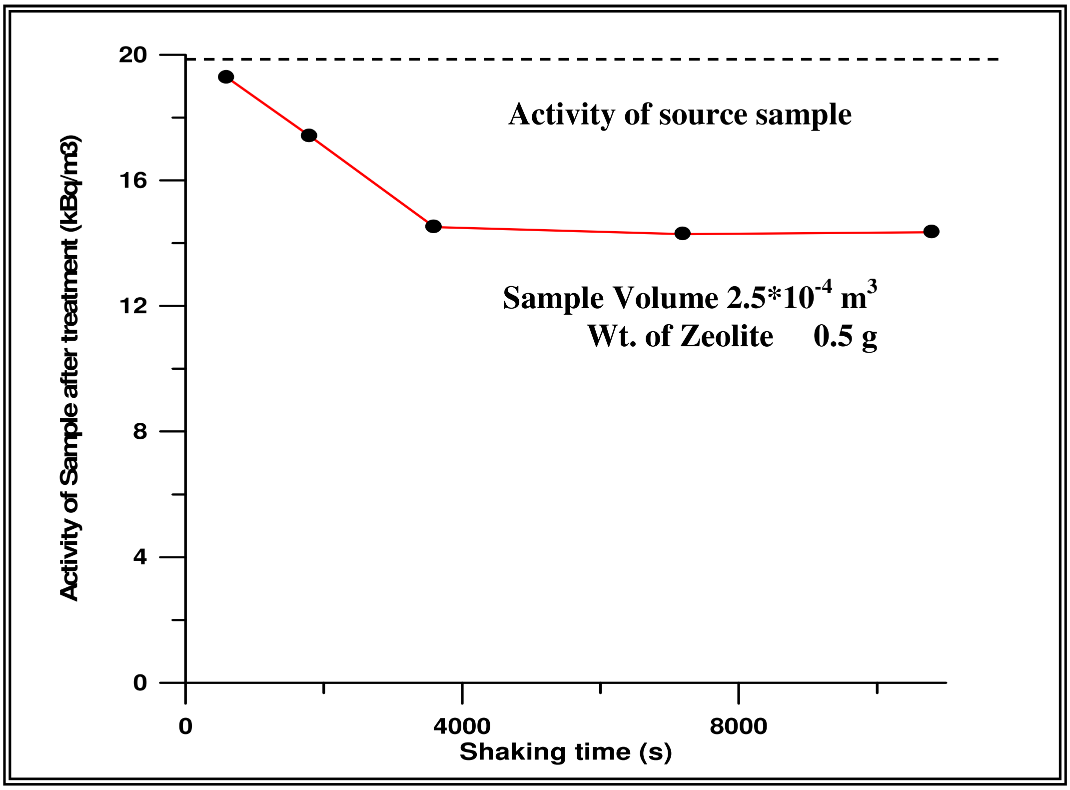

Fig. 4: Effect of Shaking Time on Radioactivity of Sample after Treatment with Zeolite.

Distribution Coefficient, Kd_r(m^3/kg) of cobalt-60 on zeolite was calculated Appendix-E , the results were tabulated in Table 2.

The relation between the distribution coefficient with shaking time can be observed from Fig. 5.

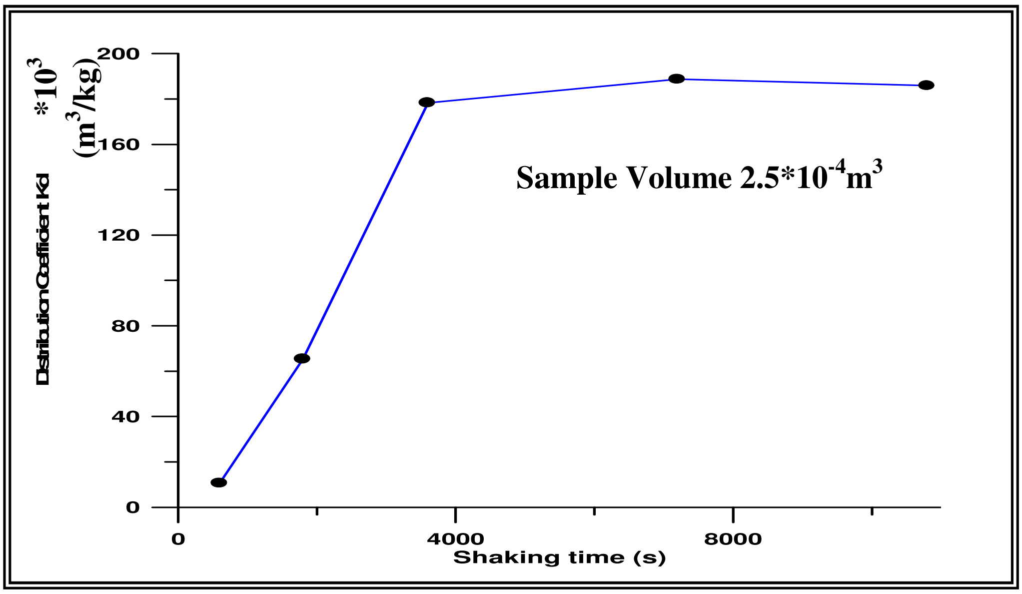

Table 3 shows a comparison between the distribution coefficient of present research and different references.

Table 3:Comparison Between Distribution Coefficient of Present Research and Different References.

Radionuclide	**Sorbent**	**Kd_r , (m^3/kg)**	**Reference**
Cobalt	Zeolite	0.16	Present Research
Cesium	Sandstone	1	Kenichi,1989
Cesium	Limestone	0.1	Kenichi,1989
Cesium and Strontium	Loam	1	Tadashi,1989
Cesium and Strontium	Bentonite	0.1	Tadashi,1989
Cesium	Bentonite (pH=2.4)	0.14	Masao,1988
Cesium	Bentonite (pH=9.3)	1.5	Masao,1988

Sorption Isotherms

Table 4 represented the radioactivity of cobalt-60 and the total concentration (radioactive and non-radioactive) after treatment with different weight of zeolite.

Table 4: Radioactivity and Atomic Concentrations of Samples.

Beaker No.	**Weight of zeolite, $*10^3$(kg)**	**Activity of Supernatant A_f (kBq/m^3)**	**Conc. of cobalt-60 $*10^{13}$ (kg/m^3)**	**C_e, Equilibrium conc. of total cobalt $*10^5$(kg/m^3)**
1	0.25	15.291	3.76	7.61
2	0.5	14.35	3.53	6.11
3	0.73	14.028	3.45	4.63
4	1.02	12.071	2.97	3.50
5	2.0	9.026	2.22	2.87

Radioactivity of sample(A_o) = 17.872 kBq/m^3
Total cobalt concentration = $9.29*10^{-5}$ kg/m^3

Table5 shows the cation exchange capacity and distribution coefficient for cobalt -60 and total cobalt.

Samples of calculation was shown in Appendix-E .

The plot of Cation exchange capacity of cobalt-60 and of total cobalt on zeolite was shown in Fig. (4-4).

Table 5: Cation Exchange C apacity and Distribution Coefficient for Cobalt-60 and Total Tobalt on Zeolite.

Beaker No.	Weight of zeolite, $*10^3$ (kg)	CEC_r $*10^4$(eq/kg) cobalt-60	Kd_r $*10^3$(m^3/kg) cobalt-60	CEC $*10^4$(eq/kg) Total cobalt	Kd $*10^3$(m^3/kg) total cobalt	x/m$*10^5$ (kg/kg)
1	0.25	4.55	168.8	5.7	220.8	1.68
2	0.5	3.1	122.7	5.4	260.2	1.59
3	0.73	2.3	98.3	5.4	345.5	1.6
4	1.02	2.5	117.8	4.8	405.7	1.42
5	2.0	1.95	122.5	3.9	383.3	1.15

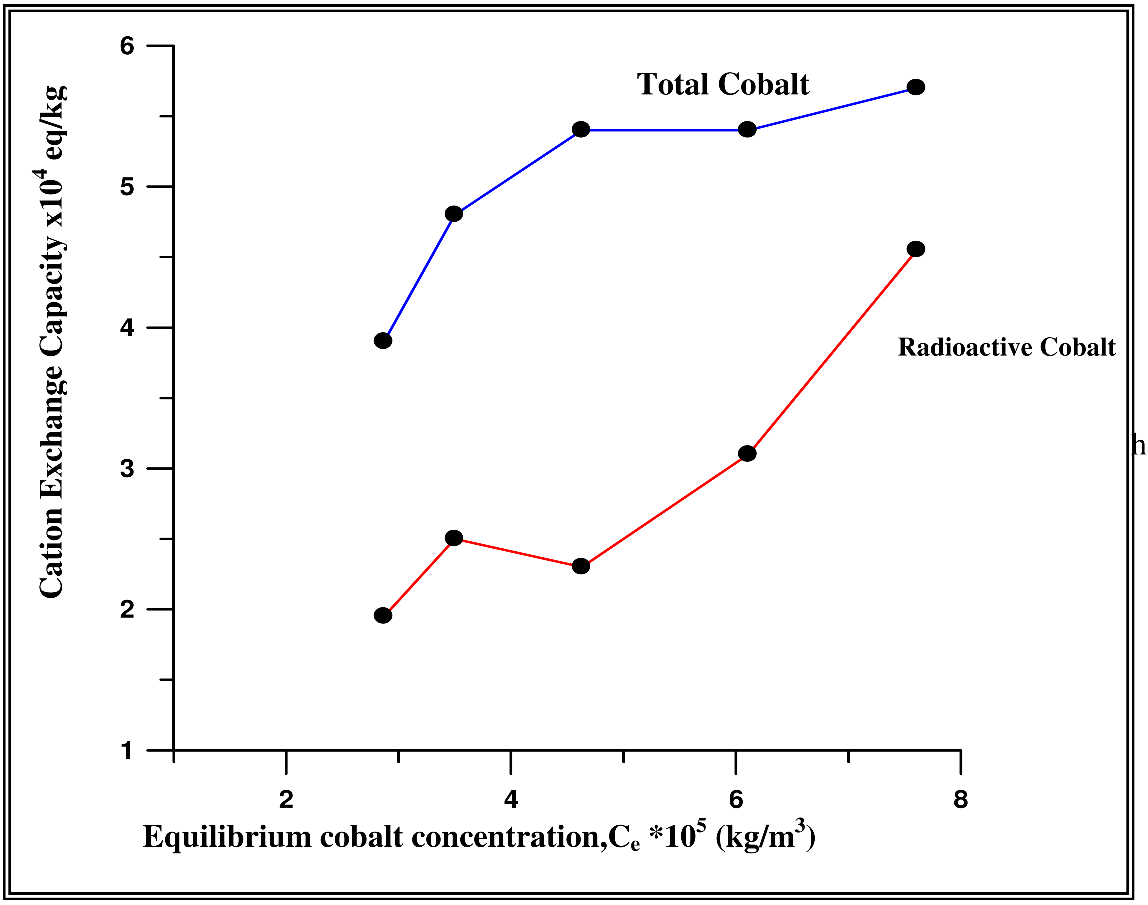

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Fig. 6: Cation Exchange Capacity of Cobalt-60 and of Total Cobalt on Zeolite.

Fig. 7: Distribution Coefficients of Total Cobalt on Zeolite.

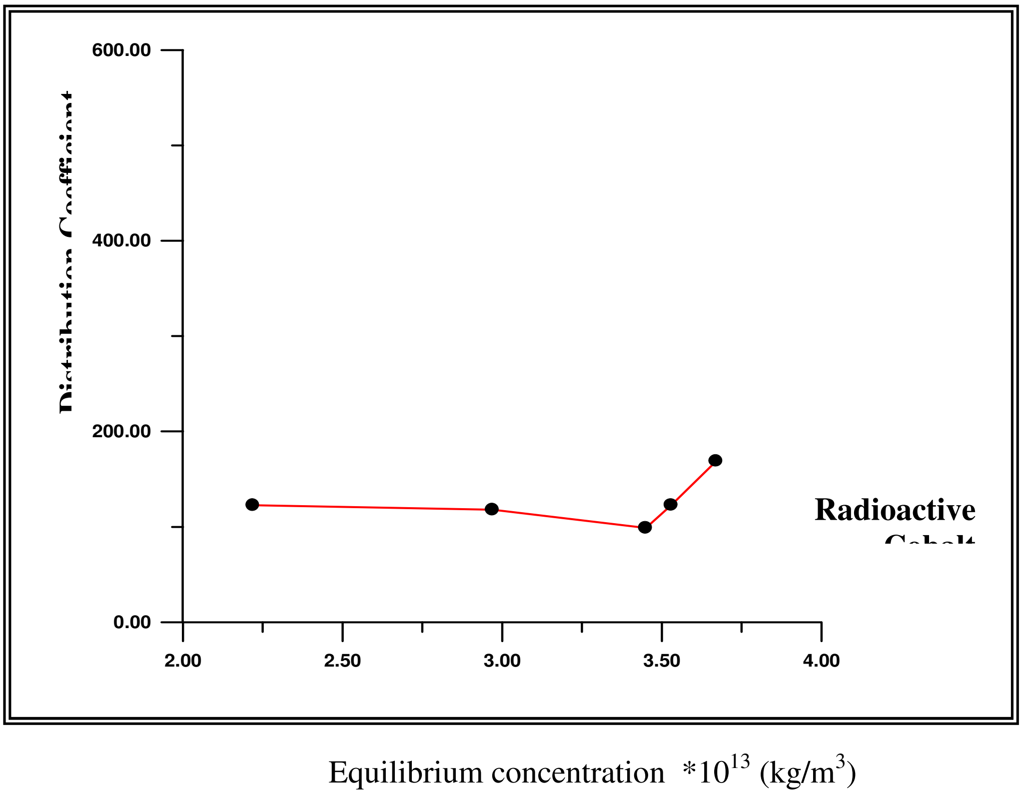

Fig. 8: Distribution Coefficients of Cobalt-60 on Zeolite.

Sorption isotherm was shown in Fig. 9.

This figure shows that the equilibrium isotherm is of the favorable type.

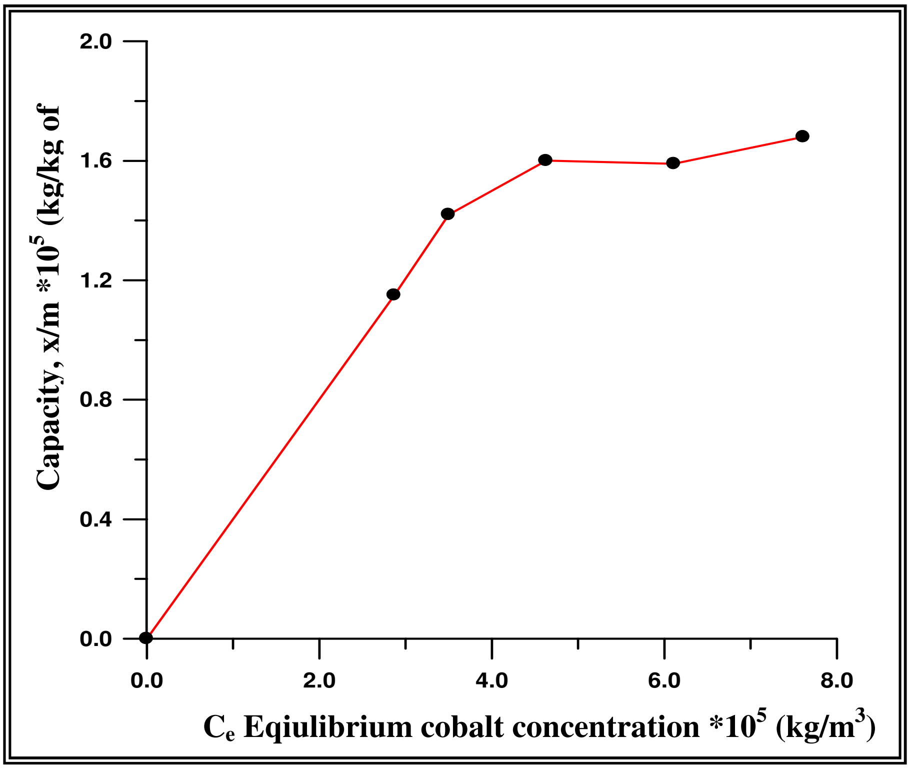

Fig. 9: Sorption Isotherm for total cobalt.

The plot of $C_e/\frac{x}{m}$ versus C_e showed a straight line in Fig. 10.

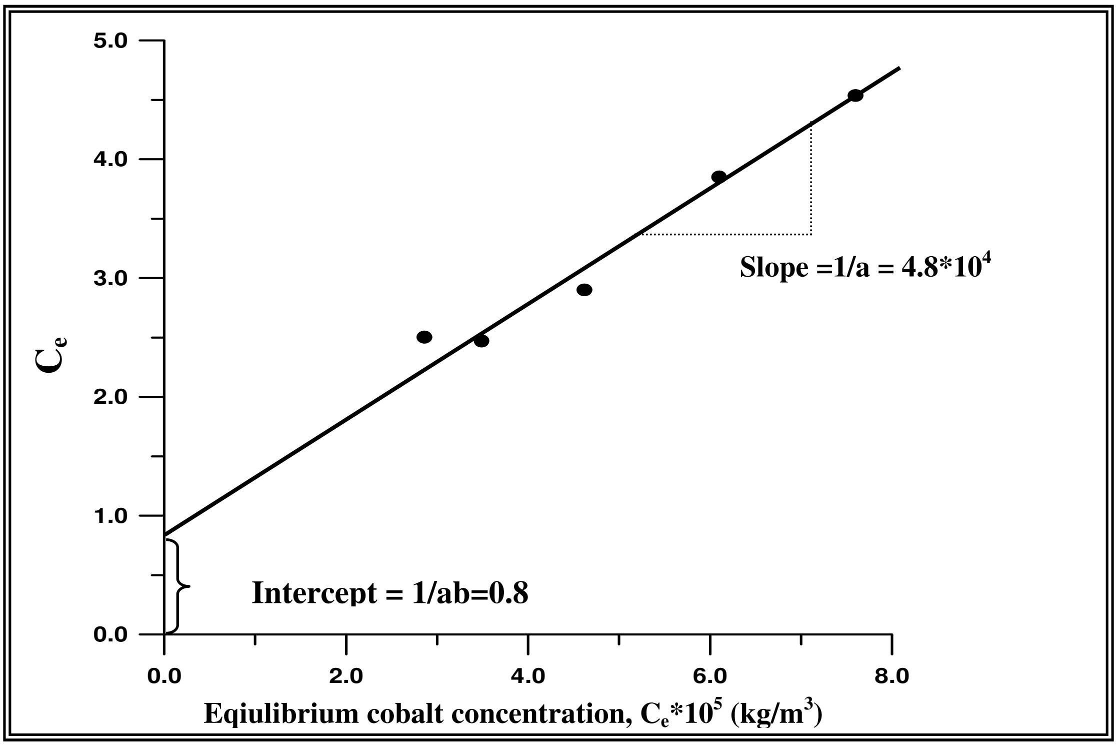

Fig. 10: Parameters for the Langmuir's Equation.

This means that the equilibrium results correlated well with Langmuir equation. Langmuir equation constants (a) and (b) were calculated from the slope and the intercept of the straight line . These values are tabulated in Table (4-5).

Langmuir's equation is:

$$\frac{x}{m} = 1.25\ C_e / (1+6x10^4\ C_e) \qquad (2)$$

The plot of ($\log \frac{x}{m}$) versus ($\log C_e$) for the same equilibrium results showed a straight line Fig. 11. This means that the equilibrium data also correlated well to Freundlich equation.

The Freundlich equation constants (K_f) and (1/n) were calculated from the slope and intercept of the straight line Fig. 11. Their values were tabulated in Table 6.

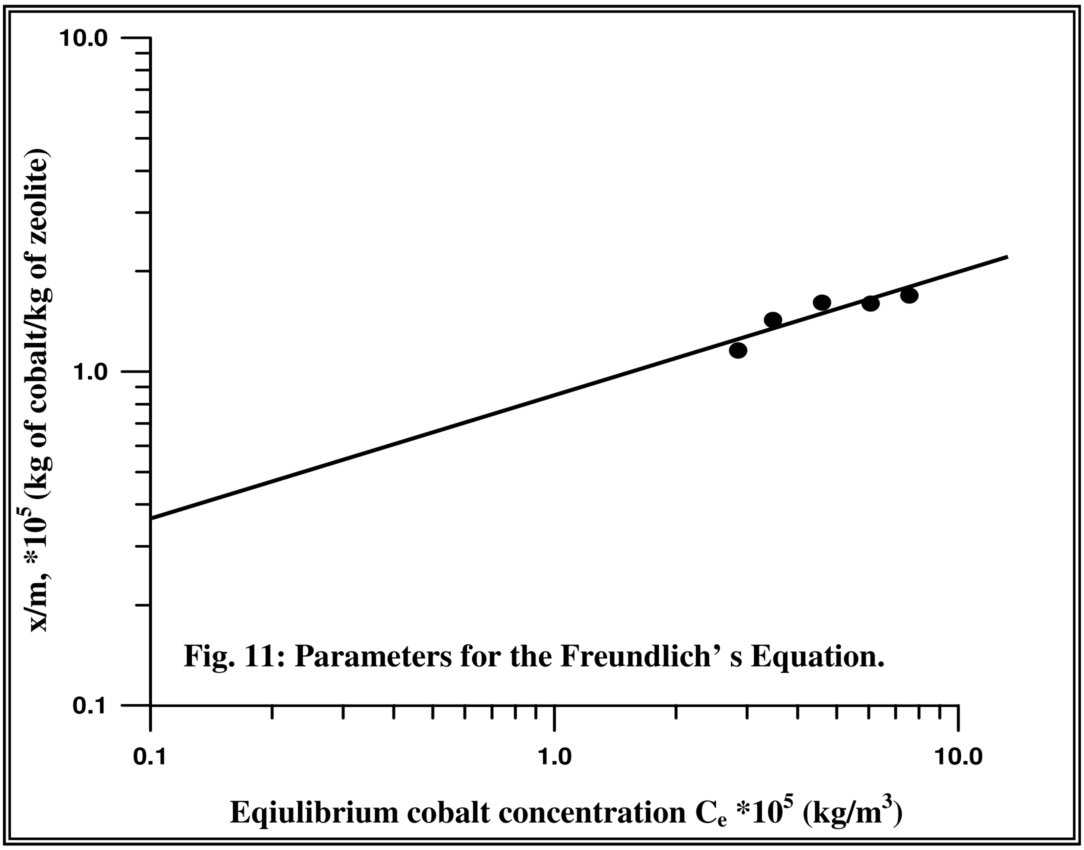

Fig. 11: Parameters for the Freundlich' s Equation.

Freundlich equation was:

$$\frac{x}{m} = 8*10^{-4}\, C_e^{0.4} \qquad (3)$$

Table 6: Langmuir and Freundlich Equation Constants.

Equation	a	b	K_f	1/n
Langmuir	$2.08 *10^{-5}$	$6 *10^{4}$	-	-
Freundlich	-	-	$5*10^{3}$	0.4

Fig (4-10) shows the comparison between the experimental, Langmuir and Freundlich isotherms.

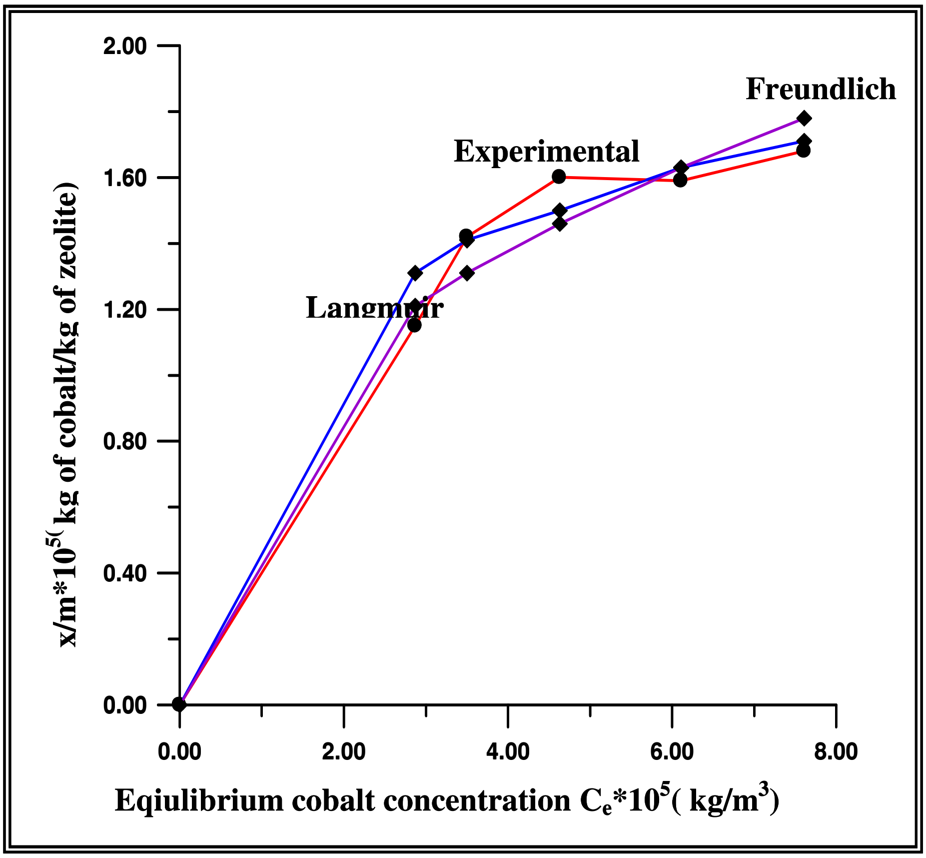

Fig. (4-10): A Comparison Between Experimental ,Langmuir and Freundlich Isotherms.

Fig. : E% and Rms for Langmuir and Freundlich.

Equation	Correlation	E%	Rms
Langmuir	$\frac{x}{m}$ = **1.25 C_e / (1+6*10^4 C_e)**	0.019	0.00047
Freundlich	$\frac{x}{m}$ = **8*10^{-4} $C_e^{0.4}$**	0.039	0.0022

where:

$$E\% = \left(\frac{1}{m}\right)\sum_{i=1}^{m}\left\{\frac{\left|Ci_{\exp.} - Ci_{calcu.}\right|}{Ci_{\exp.}}\right\}$$

$$Rm_S = \sqrt{\frac{\sum_{i=1}^{m}\left\{\left(Ci_{\exp.} - Ci_{calcu.}\right)^2\right\}}{m}}$$

Where:

E% is the absolute mean error.

Rms is the root mean square

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