



Treatment of radioactive liquid waste (Co-60) by sorption on Zeolite Na-A prepared from Iraqi kaolin

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ABSTRACT

Iraqi synthetic zeolite type Na-A has been suggested as ion exchange material to treat cobalt-60 in radioactive liquid waste which came from neutron activation for corrosion products. Batch experiments were conducted to find out the equilibrium isotherm for source sample. The equilibrium isotherm for radioactive cobalt in the source sample showed unfavorable type, while the equilibrium isotherm for the total cobalt (the radioactive and nonradioactive cobalt) in the source sample showed a favorable type. The ability of Na-A zeolite to remove cobalt from wastewater was checked for high cobalt concentration (822 mg/L) in addition to low cobalt concentration in the source sample (0.093 mg/L). A good fitting for the experimental data with Langmuir equilibrium model was observed. Langmuir constant q_m which is related to monolayer adsorption capacity for low and high cobalt concentration was determined to be 0.021 and 140 mg/g_{zeolite}. The effects of important design variables on the zeolite column performance were studied these include initial concentration, flow rate, and bed depth. The experimental results have shown that high sorption capacity can be obtained at high influent concentration, low flow rate, and high bed depth. Higher column performance was obtained at higher bed depth. Thomas model was employed to predict the breakthrough curves for the above variables. A good fitting was observed with correlation coefficients between 0.915 and 0.985.

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1. Introduction

There are many sources of low- and intermediate-level radioactive liquid waste in Alutwatha site in Iraq, those include radiochemical, radiomedical and reactors wastes. All these activities were stopped after the war at 1991. 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 came from reactor pool. The pollutant cobalt-60 in the liquid waste came from neutron activation for corrosion products. Cobalt is a major contributor toward the radiation build-up problem because of its rather long half-life ($t_{1/2} = 5.27$ y) and high energy (sum peak of 2.5 MeV) gamma emission.

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.

Ion exchange process is considered as one of the more effective methods for the removal of radioisotopes from liquid waste. 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 with no permanent changes in the structure of the solid. Compared with other separation methods ion exchange has a number of advantages and limitations. The immediate reason for their use in the nuclear industry is the comparative simplicity, of operation and the associated equipment involved, together with their high efficiency and the possible volume reduction. A limitation of ion exchange is its unsuitability for use with substances without charge as in the case in many complexes and for particles of the colloidal type. Many researchers are utilized different materials to remove metal radionuclides from aqueous radioactive wastes by ion exchange process in preparation for their final disposal [1–5].

The low cost of natural and synthetic zeolite makes their use attractive in water treatment applications. 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 [6–9]. The principle

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Table 1
Zeolite composition.

Element	Percentage (%)
SiO ₂	34.48
Al ₂ O ₃	29.94
L.O.I.	15.05
Na ₂ O	13.4
CaO	2.52
TiO ₂	1.70
Fe ₂ O ₃	0.95
MgO	0.08
K ₂ O	0.03

reason for using zeolite in radioactive waste treatment is their high selectivity and resistance to degradation from radiation. Synthetic type Na-A zeolite as crystalline with molecular formula Na₂O:0.79, Al₂O₃:1, SiO₂:1.95, powder and pellets are prepared in Iraqi Atomic Energy Commission (IAEC) Laboratories was used as material under investigation in this study. After the zeolite has been exhausted in the treatment of radioactive liquid waste, there is no regeneration and it will be disposed as radioactive solid waste. The zeolite with retained radioactivity must be immobilized by cementation as final process for disposal [10,11]. Zeolite amounts in weight up to 10% of cement amount did not cause any weakness on the strength of cemented matrix [12,13].

The aim of this research is to investigate the performance of Iraqi Na-A zeolite in the treatment of radioactive liquid waste contained Cobalt-60 by batch and fixed bed ion exchange experiments. Different variables in fixed bed experiments (concentration, flow rate and bed depth) were studied. Thomas model was applied to predict the breakthrough curves for ion exchange, and to determine the characteristic parameters useful in design using nonlinear regression.

2. Materials and methods

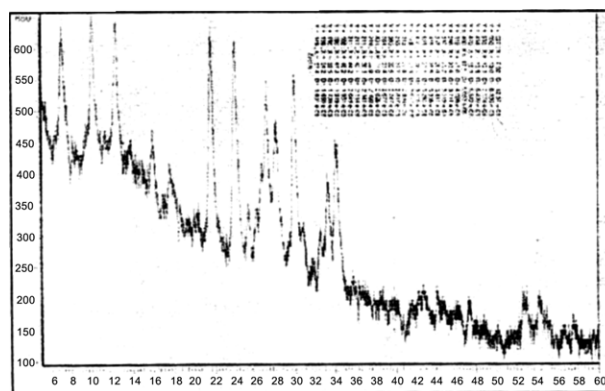
2.1. Adsorbent

Zeolite was used as sorbent, it is of type A in the sodium form (Na-A). Zeolite in crystalline powder form was prepared at Iraqi Atomic Energy Commission (IAEC) laboratories [14]. This material was prepared from Iraqi Kaolin (from Kaara region). It treated with 2 N sodium hydroxide solution at boiling point under agitation for 2 h. Pellets were formed by mixing the product with natural kaolin in specific proportion as cross linking material. These pellets were calcined in the furnace at 600 °C for 3 h for solidification. Zeolite in crystalline powder form was used in batch system experiments, whereas the pellet form was used in continuous system experiments. Elemental analysis was accomplished in the Geological Survey and Mining Company's Laboratories. The composition of zeolite is shown in Table 1. The physical properties of zeolite pellets are listed in Table 2.

X-ray diffraction and infrared scanning were performed in Geological Survey and Mining Company's Laboratories (Figs. 1 and 2). The results were found to be coincided with type Na-A zeolite which was used throughout the research.

Table 2
Physical properties of zeolite pellets.

Dimension	2 mm × 6 mm
Bulk density	0.58 g/cm ³
Particle density	2.38 g/cm ³
Internal porosity	0.3
Void fraction of bed	0.756
Surface area	7.82 × 10 ⁴ cm ² /g

**Fig. 1.** X ray diffraction for Na-A zeolite.

2.2. Adsorbate

Two types of liquid waste were used in the present research:

- Radioactive liquid waste (the source sample) collected with the aid of health physics team from the reactor pool. The samples contained Co-60 from neutron activation of corrosion product. This type of liquid waste was used in the batch experiments.
- Simulated waste solutions were prepared from cobaltous oxide (CoO carrier free of Co-60) supplied by BDH chemical Ltd. Pool/England (M_{wt} . equal to 74.93 with 99.9% purity). Deionized water with electrical conductivity of less than 3 μ siemens/cm was used to prepare the solutions. This type of liquid waste was used in the column experiments.

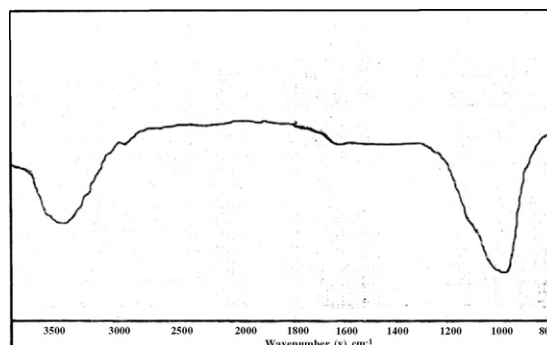
2.3. Equipments

Gamma spectrometry (Canberra-USA) with sodium iodide scintillation detector was used to analyze the radioactivity concentration of the samples, and the atomic adsorption spectrophotometry (A.A-6200 Shemadzu, Japan), flame emission type, was used to analyze the total cobalt concentration of samples (radioactive and nonradioactive).

2.4. Batch experiments

Batch experiments were used to study the sorption rate and sorption isotherm of cobalt-60 on synthetic type Na-A zeolite.

To determine the sorption rate, 250 mL of radioactive liquid waste (the source sample with radioactivity of 19.684 Bq/L) was placed into five beakers of 1 L size. Accurately weighted amount of zeolite powder (0.5 g) was added to these beakers. Each beaker was sealed with parafilm and placed in an oscillating shaker (90 rpm).

**Fig. 2.** Infrared scanning for Na-A.

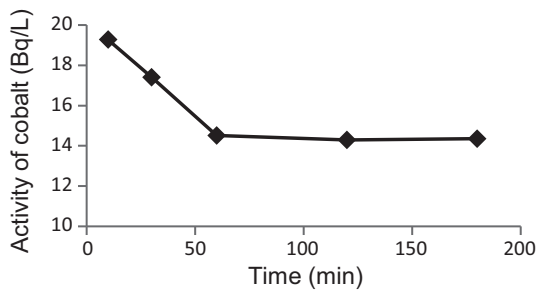


Fig. 3. Sorption rate for radioactive cobalt on zeolite.

Each beaker was shaken for a various periods of time (10, 30, 60, 120, and 180 min). After shaking, the contents were distributed into six closed plastic ampoules, and then placed in a centrifuge (10,000 rpm) for 30 min. The supernatant of all ampoules were collected into 1 L beaker and then transferred to special container to analyze in gamma spectrometry scintillation detector. The results have shown that 1 h is sufficient for reaching equilibrium (Fig. 3).

To determine the sorption isotherm for low cobalt concentration, 250 mL of radioactive liquid waste (the source sample with radioactivity of 17.872 Bq/L) was placed into five 1 L beakers. Accurately weighted amounts of zeolite powder (0.25, 0.5, 0.73, 1.02, and 2.0 g) were added to these beakers. Each beaker after sealing by parafilm was placed in an oscillating shaker (90 rpm) for 4.5 h to reach equilibrium. The content of each beaker was distributed into six closed ampoules, and then placed in a centrifuge (10,000 rpm) for 30 min. The supernatant was collected into (1 L) beaker, after that it transferred to special container to be analyzed using Gamma Spectrometry Scintillation Detector. Concerning high cobalt concentration simulated waste solution was used. The zeolite powder weights that used in the experiments were (0.5, 1, 2, and 3 g). The same steps for the above procedure was applied, using atomic adsorption spectrophotometry for analysis.

2.5. Column experiments

For the design of industrial scale fixed-bed sorption systems, column operations are an absolute must. Column experiments were carried out at different variables, concentration, flow rate, and bed depth to study the performance of synthetic type Na-A zeolite pellets in removing cobalt from liquid waste.

Glass column of 1 cm (I.D.) and 30 cm height was used. The zeolite was confined in the column by fine stainless steel screen at the bottom. Two containers were used; the first one as feed container while the second one as receiver. After preparing the desired concentration in the feed container the solution was pumped through the bed. The concentration of the cobalt in the samples was determined by means of atomic adsorption spectrophotometer.

3. Results and discussion

3.1. Source sample analysis

Radioactive liquid wastes (source samples) were analyzed in gamma spectrometry scintillation detector (NaI) sodium iodide type. The analytical graph is presented in Fig. 4. It was observed that the radioactivity of the sample came from cobalt-60 presented in the reactor coolant by neutron activation of corrosion products. Two source samples were used for batch experiments. The analysis of the source sample which used for sorption rate experiments was found to be of concentration 19.684 Bq/L (4.79×10^{-10} mg/L radioactive cobalt). The analysis of the source sample which used for sorption isotherm experiments

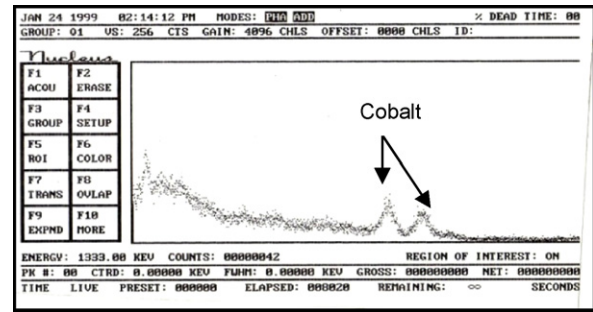


Fig. 4. Analytical graph for source.

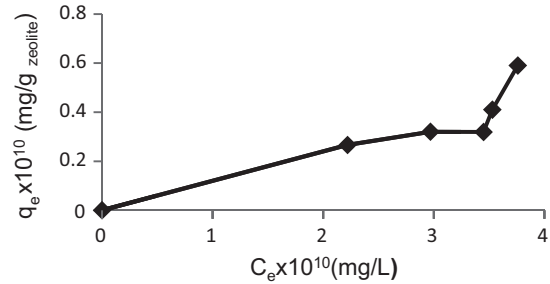


Fig. 5. Sorption isotherm for radioactive cobalt in source sample on zeolite.

was found to be of concentration 17.872 Bq/L (4.35×10^{-10} mg/L radioactive cobalt), this sample was analyzed by atomic adsorption spectrophotometry. The results have shown that total cobalt concentration (radioactive and nonradioactive) was 0.093 mg/L.

3.2. Sorption isotherms

Fig. 5 shows the adsorption isotherm for radioactive cobalt in the source sample, it is of unfavorable type, while Fig. 6 shows the adsorption isotherm for total cobalt (radioactive and nonradioactive cobalt) in the source sample, it represents the favorable type of adsorption isotherm.

The ability of zeolite to remove cobalt from wastewater was checked for high cobalt concentration (822 mg/L), in addition to the low concentration (0.093 mg/L in the source sample). Fig. 7 shows the adsorption isotherm for high cobalt concentration. A favorable type of adsorption isotherm can be observed from this figure.

Langmuir equation was applied to the sorption isotherms for low and high concentration of cobalt:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (1)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent at C_e (mg/g), q_m is Langmuir constant related to monolayer adsorption capacity

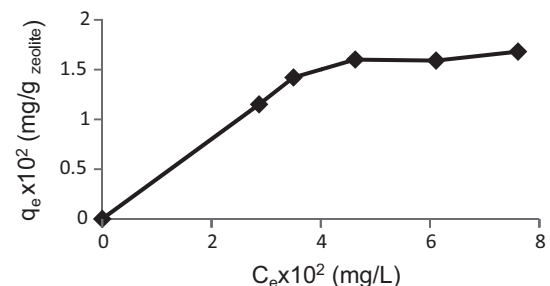


Fig. 6. Sorption isotherm for total cobalt sample on zeolite.

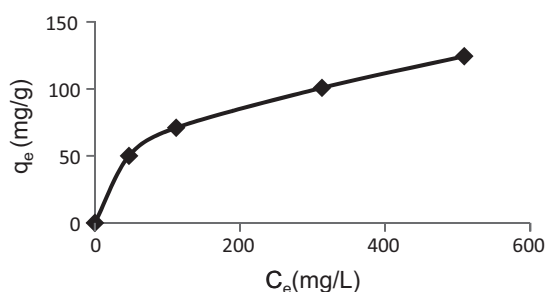


Fig. 7. Sorption isotherm for high cobalt concentration on zeolite.

Table 3
Langmuir constants for low and high concentration.

Concentration (mg/L)	q_m (mg/g _{zeolite})	b (L/g)	R^2	
Low	0.093	0.021	6×10^4	0.97
High	822	140	9.5	0.98

(mg/g), and b is Langmuir constant related to the energy of adsorption (L/mg).

Langmuir constants were determined from the slope and the intercept of the straight line when plotting C_e/q_e vs. C_e . The Langmuir constants were listed in Table 3, the correlation coefficients are 0.97 and 0.98. From Table 3, it can be observed that high monolayer adsorption capacity (140 mg/g_{zeolite}) for high cobalt concentration is so high compared with monolayer adsorption capacity (0.021 mg/g_{zeolite}) for low cobalt concentration.

The increase in uptake capacity of Zeolite material with the increase of initial cobalt concentration may be due to higher probability of collision between cobalt ion and Zeolite. Also the driving force for sorption process was increased due to high concentration gradient at high cobalt concentration.

3.3. Fixed bed experiments

Fixed bed sorption experiments were carried out to study the sorption dynamics. The effects of process variables on the zeolite column performance were studied. These variables include initial concentration, flow rate, and bed depth (Table 4). The breakthrough curves (the concentrations of cobalt in the effluent C vs. t), and the rate of sorption curves (cobalt adsorbed per unit mass of zeolite q vs. t) for the above variables were plotted (Figs. 8–13).

3.4. Effect of initial concentration

Experiments with different initial concentrations (3, 5, and 7 mg/L) were carried out at fixed flow rate 2.5 mL/min and bed depth 3.5 cm.

Fig. 8 shows the breakthrough curve for the above concentrations. It can be observed that the breakthrough point (which is a point on the breakthrough curve where the effluent concentration reaches the maximum allowable concentration) appears earlier for highest initial concentration. This happens because the binding

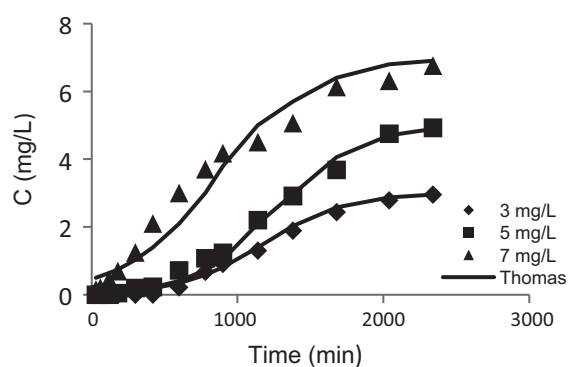


Fig. 8. The breakthrough curves at different concentrations.

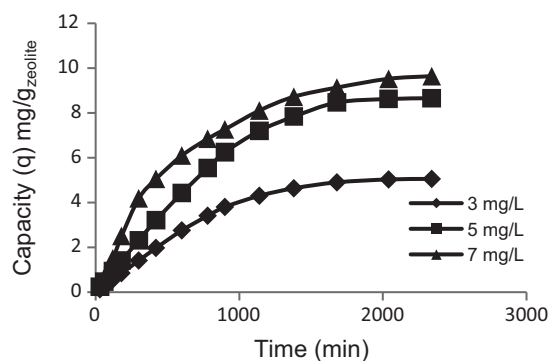


Fig. 9. Rate of sorption at different concentrations.

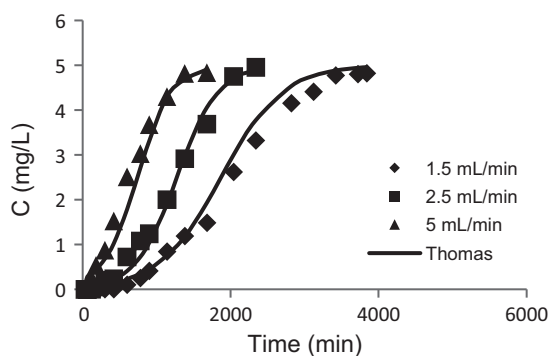


Fig. 10. The breakthrough curves at different flow rates.

sites and the ion exchange sites become quickly saturated for high concentrations and the primary adsorption zone mobilized rapidly across the bed.

Fig. 9 shows the rate of sorption for the above concentrations. Apparent increase in the sorption capacity was observed for high concentration.

Table 4
Fixed bed experimental data and Thomas model parameters.

C_o (mg/L)	Q (mL/min)	Z (cm)	Bed capacity (mg/g _{zeolite})	Column performance (%)	K_{Th} (mL/mg/min)	q_o (mg/g)	R^2
3	2.5	3.5	5.05	46	1.2	5.6	0.985
5	2.5	3.5	8.64	47.3	0.72	10.1	0.976
7	2.5	3.5	9.64	38	0.43	10.4	0.915
5	1.5	3.5	8.94	50	0.36	11.4	0.982
5	5	3.5	8.2	32	0.84	11.5	0.955
5	2.5	4.5	8.94	52.2	0.62	10.2	0.976
5	2.5	5.5	9.2	59	0.6	10.4	0.979

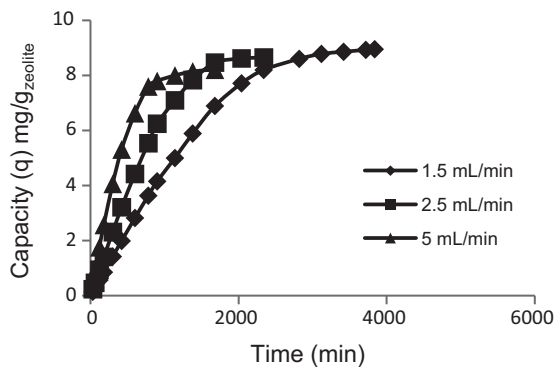


Fig. 11. Rate of sorption at different flow rates.

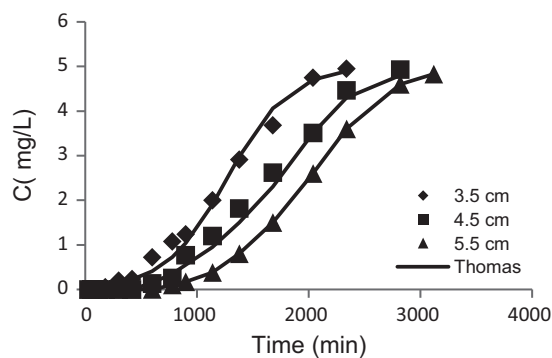


Fig. 12. The breakthrough curves at different bed depths.

3.5. Effect of flow rate

Experiments with different flow rates (1.5, 2.5, and 5 mL/min) were carried out at fixed initial concentration 5 mg/L and bed depth of 3.5 cm.

The breakthrough and the rate of sorption curves were shown in Figs. 10 and 11. It can be noticed that the breakthrough point appears earlier for the highest flow rate (Fig. 10). At earlier period of experiment the uptake of cobalt is high for the highest flow rate, but earlier saturation leads to lower capacity. The uptake at low flow rate continues to longer period of time leads to high capacity (Fig. 11). For low flow rate the mobile phase spent greater time with the solid surface of stationary phase, the primary adsorption zone mobilized slowly across the bed in the column, hence later saturation of the bed can be achieved. A linear portion exists for each curve at early period of experiments (Fig. 11). The linear portion of the curve indicate that the film diffusion controls as rate limiting step to a point at which the external surface area becomes

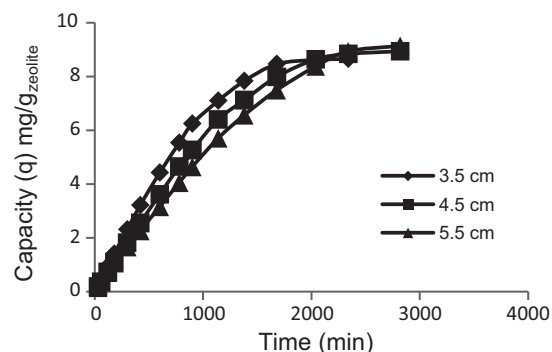


Fig. 13. Rate of sorption at different bed.

essentially saturated, and deviation from linearity occur because of the increasing influence of intraparticle transport on the overall rate of mass transfer as each run progresses. The linear segment of the curve extended over a shorter period of time for high flow rate and steeper curve was observed leading to fast saturation of bed. Insufficient residence time of the solute in the column may limit the diffusion through the pores.

3.6. Effect of bed height

Experiments with different bed depths (3.5, 4.5, and 5.5 cm) were carried out at fixed initial concentration 5 mg/L and flow rate of 2.5 mL/min.

The total bed depth must be larger than the primary adsorption zone otherwise the breakthrough point cannot be identified at the breakthrough curve. From Fig. 12 the breakthrough point appears later for highest bed depth, since increasing bed depth provide extra surface area for sorption process to carry on, allowing more than one primary sorption zone to be appeared. Fig. 13 shows nearly the same uptake at early period of experiment then sequential saturation was attained beginning from the lower bed depth. Referring to Table 4, it can be noticed that high percent of column performance ((the amount of cobalt retained in the column)/(amount of cobalt inter the column) × 100) was obtained at high bed depth 5.5 cm. While the maximum sorption capacity obtained at high cobalt concentration 7 mg/L.

4. Modeling the break through curve

The most important criterion in the design of fixed bed sorption systems is the prediction of breakthrough curve, which determines the operation life span of the bed. Thomas model is one of the most general and widely used methods in column performance theory. It gives a general analytical solution for the differential equations that describe the transport of fluid in fixed bed sorption process with nonlinear equilibrium relationship. Thomas model is based on second order reaction kinetics. The equilibrium relationship is assumed to be of Langmuir (favorable) isotherm model. Thomas excludes the effect of axial dispersion. When the sorption isotherm is highly favorable, the actual Thomas model is reduced to the Bohart-Adams model [15]:

$$\frac{C}{C_0} = \frac{1}{1 + \exp((K_{Th}q_0M/Q)K_{Th}C_0t)} \quad (2)$$

where K_{Th} is the kinetic coefficient (mL/mg/min), q_0 is the maximum (equilibrium) sorption capacity of the bed (mg/g), M is the mass of adsorbent packed in the column (g), Q is the flow rate (mL/min), C and C_0 are the concentrations of cobalt in the influent and in the effluent at any time t .

The linearized form of the above equation is as follows:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{K_{Th}q_0M}{Q} - K_{Th}C_0t \quad (3)$$

The kinetic coefficient K_{Th} and the equilibrium sorption capacity of the bed q_0 can be determined from a plot of $\ln((C_0/C) - 1)$ against t at a given conditions for the fixed bed.

Figs. 8, 10 and 12 show that the Thomas model gives a good fit of the experimental data. The value of K_{Th} and q_0 are given in Table 4. It can be observed that q_0 increases as cobalt concentration increases. High value of q_0 was obtained at low flow rate 1.5 mL/min. In addition high value of q_0 was obtained at high flow rate 5 mL/min, this may be due to high uptake in early period of experiment. No apparent difference in q_0 for different bed depths. K_{Th} decreases with the increase in cobalt concentration and bed depths while it increases with the increase of flow rate.

5. Conclusion

Based on the experimental results, the following conclusions can be drawn:

Synthetic Iraqi Na-A zeolite can be used to removal cobalt-60 from radioactive liquid waste. Equilibrium isotherm for radioactive cobalt in the source sample shows unfavorable type, while the total cobalt in the source sample shows a favorable type. Langmuir model were successfully modeled the sorption data. The Langmuir constant q_m for low and high cobalt concentration was determined to be 0.021 and 140 mg/g_{zeolite}, respectively, which represent the mono layer capacity. The fixed bed column sorption experiments show that high sorption capacity can be attained at high influent concentration, low flow rate, and high bed depth. In the present research, the highest sorption capacity was obtained at high initial cobalt concentration while the highest percent of column performance was obtained at high bed depth. Good fitting of the experimental data and Thomas model was obtained with correlation coefficient of 0.915–0.985.

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