

COBALT ADSORPTION/DESORPTION ON SEDIMENTS FROM PIRAQUARA DE FORA BAY, ANGRA DOS REIS

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ABSTRACT

Among the radionuclides released with the liquid effluents from PWR power plants, cobalt isotopes (⁶⁰Co and ⁵⁸Co) play an important role for risk and environmental impact assessments. The laboratory experiments on radionuclide adsorption-desorption, followed by the use of adsorption isotherms are useful tools for prediction of transport, distribution, accumulation, and fate of a contaminant into a specific medium. Adsorption and desorption experiments were carried out in batches, using two sediment samples collected in Piraquara de Fora Bay, near the discharge channel of the liquid effluents from CNAAA. Aiming the assessment of the radioisotope adsorption mechanisms, sediment samples were shaken with solutions containing cobalt chloride which concentrations ranged between 10⁻¹⁰ and 10⁻³ M. In order to estimate the efficiency of adsorption, 100 Bq of ⁶⁰Co were used as radioactive tracer. The experimental data fitted well with Freundlich and Langmuir isotherms. Results point out a favorable and high cobalt adsorption on the sediments, although smaller than the ones reported in literature studies. Such smaller trend of adsorption coefficients may be caused by the low exchange capacity of the prevailing clay, kaolinite. The maximum adsorption capacities were found to be 10 and 17 moles/g for sediments in PT-01 and PT-02, respectively. Values lower than 8% of the adsorbed cobalt underwent desorption and this amount decreased to 4%, with time, which show the high retention capacity of these sediments.

1. INTRODUCTION

The Central Nuclear Almirante Álvaro Alberto (CNAAA) - located in the Itaorna Bay, Angra dos Reis, Rio de Janeiro State, Brazil - comprises a complex of three pressured water power plants, named Angra I e Angra II – operational since 1985 and 2000, respectively – and Angra III, presently under construction. The purpose of CNAAA is power generation, though, as in any other power plant, fission products are secondarily produced, being then storage or, after a suitable treatment, released to the environment as liquid and gas effluents.

The cooling water for the CNAAA power plants - used for the condensation of exhaustion vapors from the low pressure turbines – is primarily obtained in Itaorna Bay, being lately directly released through a 1 km length pipeline into the Piraquara de Fora Bay (PFB), at an overall flow of 120 m³.s⁻¹ and a temperature around 40°C [1,2]. Due to this liquid effluent release in PFB, an increase of around 7°C in the water temperature of the bay is foreseen [3]. Among other radionuclides, ⁶⁰Co is released in the liquid effluents from the power plants.

An assessment performed by LAURIA *et al* (2011) [4], using the database provided by the environmental monitoring program executed by the Instituto de Radioproteção e Dosimetria (IRD) (between 1985 and 2010) pointed out the occurrence of ^{60}Co in sediments from sampling points (PT-01 and PT-02) of PFB. Besides, the ^{60}Co levels in the sediments presented relevant variations overtime. Between 1985 and 2000, PT-01, the sample point closest to the liquid effluents discharge point, presented higher containing of ^{60}Co than PT-02. However, a reversed behavior was observed from 2000 on, when the radionuclide concentrations in PT-02 started to surpass those observed in PT-01.

Therefore, a project was drawn up, aiming to study the sorption mechanisms of the sediments, which should provide some issue about the reasons that led to such unexpected behavior. The first stage comprised the physical and chemical characterization of the sampled sediments in both points and the determination of the distribution coefficient values for ^{60}Co , already issued [5]. The present study aims the assessment of ^{60}Co adsorption/desorption rates for PT-01 and PT-02 sediments, to compare the radionuclide adsorption behavior on the sediments and to estimate their maximum adsorption capacities by means of adsorption isotherms.

1.1. Adsorption Isotherms

The adsorption kinetics of absolute on an adsolvent matrix may be assessed by correlating the equilibrium curves. Among all isotherm models applied in the description of the nature of the equilibrium, the Freundlich and Langmuir versions are mostly used [6].

For highly heterogeneous surfaces, the Freundlich Isotherm can be used to describe the adsorption, while being valid for a restricted concentration range that rules out very low concentrations, to which Henry's law is valid. The Freundlich model assumes the occurrence of adsorption on multilayer phase of the adsorbent. The determination of slope and intercepts of linear graphs enables to estimate K_F - the constant of Freundlich isotherm - and $1/n$ - the Freundlich isotherm exponent constant -both related to the adsorption intensity. K_F values are related to the surface heterogeneity, and the closer it gets to unity, the less heterogeneous the surface [7].

In its turn, Langmuir Isotherm is valid for homogeneous surface and considers as identical and defined all the adsorbent active sites. Since each site retains only one solute molecule adsorption takes place in a single layer of solute molecules on the adsorbent (monolayer type) [8]. The Langmuir isotherm follows the Henry's law at a large range of concentrations. Relevant parameters as K_L - related to the apparent energy of adsorption and R_L - which evaluates the monolayer adsorption capacity – can be calculated from both the linear equation and subsequent angular and linear coefficients. R_L values ranging between 0 and 1 point out a favorable adsorption. Besides, the maximum adsorption capacity of the adsorbent can be also assessed, corresponding to complete monolayer coverage on the adsorbent.

In the construction of the isotherm, it is essential to determine the time interval required to solute-adsorbent system or solute adsorption reach an equilibrium condition, so that the concentration of the solute, which remains in the aqueous phase at the equilibrium (C_{eq}), can be calculated. The experiment is performed by determining the concentration of solute in the aqueous phase and on the adsorbent, after contacting the solid-liquid system at a required time period for the establishment of equilibrium, using a wide range of initial solute concentrations.

The isotherms assessment can be also used to estimate thermodynamic parameters, which provides information about the nature of adsorption (if endothermic or exothermic), the spontaneous adsorption reaction and its relationship with temperature [9].

2. MATERIAL AND METHODS

Initially, water and sediment samples were collected in two monitoring sampling points – here named PT-01 and PT-02 – established through a survey of the overall researched area– and belonging to the impacted section, defined as the most feasible to accumulate metals. The samples were collected in the Piraquara de Fora Bay (PFB), PT-01 (S23° 00.778; W44° 26.598) and PT-02 (S23° 00.840; W44° 26.493), by means of a Van Veen manual bottom sampler and a Van Dorn bottle sampler. Figure 1 shows the sampling locations. Afterwards, the samples were transferred and kept under refrigeration at the Instituto de Radioproteção e Dosimetria (IRD).



Figure 1: Location of the CNAAA and the sediment sampling points.

Later in laboratory, the sediment samples were dried in a stove at 80°C, for 48 hours, at constant weight, being then smashed and kept in room temperature. Aliquots of the sediments were then used in the laboratory experiments. In order to determine parameters such as granulometry and cationic exchange capacity, samples of the dry and smashed sediment from PT-01 and PT-02 were sent to Embrapa Solo [10].

2.1. Adsorptions Kinetics

The adsorption kinetics for ^{60}Co on the PT-01 and PT-02 sediments was evaluated with around 0.5 g sediments aliquots in 50 ml polycarbonate centrifuge tubes (Falcon), being 35 ml of PFB seawater added in each tube. Subsequently, all sediment-water samples were left to rest for one week, in such a way that the consequent hydration could replicate the local hydrological profile.

Afterward, around 100 Bq of ^{60}Co activity was added to each tube, and the samples were placed on a shaker table. After some period of time, two samples from each sediment was removed. The whole experiment last 15 days. To all sediment-water samples, pH was determined before and after agitation, and the temperature and air relative humidity were maintained around 23°C and 69%, respectively.

At the end of each period of time, the samples were centrifuged and a 30 ml aliquot of the supernatant solution were transferred to a specific plastic vessel for being analyzed by gamma spectrometry, using a Canberra hyper-pure germanium detector, with a 20% relative efficiency; the counting time was 3600 seconds. For this condition, the minimal detectable activity for ^{60}Co is $1.28 \cdot 10^{-2}$ Bq. From the results achieved by gamma spectrometry, the % of adsorbed ^{60}Co was calculated by the following equation:

$$\% A_{sed} = \frac{(A_{tot} - A_{sol})}{A_{tot}} \cdot 100 \quad (1)$$

Where:

- A_{sed} is the activity in the solid phase (Bq);
- A_{tot} is the added total activity (Bq);
- A_{sol} is the activity in the liquid phase (Bq).

2.2. Desorption Studies

For this experiment, sediment samples derived from the adsorption experiment were used. At this step, around 35 ml of PFB water were added to each tube, containing the sediments from the adsorption experiments. Next, the samples were agitated once more for different periods of time (1, 3, 5 and 8 days). The experiment took place at room temperature, around 23°C.

At the end of each period of time, the samples were removed from the shaker table and centrifuged. Next, a 30 ml aliquot of the liquid phase were transferred to plastic vessels in which the radionuclides were determined by gamma spectrometry analysis. Based on the activity of ^{60}Co on the liquid phase, it was possible to determine the percentage of radionuclide, which was desorbed from sediment and available again in the aqueous phase.

2.3. Adsorption Isotherms

A similar method was adopted to the adsorption isotherms experiments, which comprises a sediment-solution agitation, along with the use of a radioactive tracer. Nevertheless, this step included also, besides the radioactive tracer, the use of solutions with different Co concentrations, in the form of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (hexahydrated cobalt chloride).

For preparation of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ mother solution – with a 10^{-3}M concentration – a 0.2380 g mass of the reagent was weighted by means of an analytical balance. Then the salt mass was transferred to a 1 l volumetric flask, containing some distilled water. Immediately thereafter, the salt was dissolved, solution homogenized and the flask volume fulfill.

Subsequently, a 10^{-4} M solution was prepared by dilution of a 10 ml aliquot from the mother solution, which was transferred to a 100 ml volumetric flask, which was fulfilled with distilled water. The next solution preparations followed the same pathways, with subsequent 1:10 dilution of the 10^{-4} M solution to get the 10^{-5} M solution and so on. At the end, seven concentrations were prepared: 10^{-3} , 10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} , 10^{-8} and 10^{-9} M, though only 10^{-3} , 10^{-5} , 10^{-7} and 10^{-9} M concentrations were used for the adsorption isotherms experiments.

Around 0.5 g of sediment were transferred to the Falcon tubes, and then 30 ml of the cobalt solutions were added to the tubes. For each sample point, a total of 12 Co solution-sediment samples were prepared; three replicated experiment for each Co solution (10^{-3} , 10^{-5} , 10^{-7} and 10^{-9} M concentrations). As a tracer, 100 Bq of ^{60}Co was added in each tube. The tubes containing the sediment-Cosolution- ^{60}Co tracer samples were kept in hydration process for one week, in order to replicate the sampling site hydrological profile, as for the adsorption experiments above described. In addition, temperature was kept around 23°C and the relative air humidity in around 69%. Simultaneously, a blank sample consisting only of distilled water and ^{60}Co tracer was prepared, in order to assess the adsorption in the tube walls.

Afterwards, the samples were placed in the shaker table, for a 8 days period, to allow the system to achieve the equilibrium condition. After 8 days, the samples were taken out from agitation and centrifuged. An aliquot of 25 ml of the liquid phase was transferred to plastic containers. To the containers, 5 ml of distilled water were added, in order to get the counting geometry (1 cm flask). Next, the samples were analyzed by gamma spectrometry as above described.

The following equations were applied for the adsorption isotherms development:

2.3.1. Freundlich Isotherm

$$\log C_{sed} = \log K_F + \frac{1}{n} \log C_{eq} \quad (2)$$

Where:

- C_{sed} is the amount of the adsorbed contaminant in the solid matrix (moles/Kg);
- C_{eq} is the contaminant concentration in equilibrium in the solution (moles/L);
- K_F is the Freundlich adsorption coefficient (L/moles);
- $1/n$ is a coefficient related to the relative magnitude and diversity among energies related to an adsorption process

2.3.2. Langmuir Isotherm

$$\frac{C_{eq}}{C_{sed}} = \frac{1}{K_L} \cdot \frac{1}{A_m} + \frac{1}{A_m} \cdot C_{eq} \quad (3)$$

Where:

- C_{sed} is the amount of the adsorbed contaminant in the solid matrix (moles/Kg);
- C_{eq} is the contaminant concentration in equilibrium in the solution (moles/L);
- K_L is the Langmuir adsorption coefficient ;
- A_m is the maximum contaminant amount that can be adsorbed in the solid matrix.

The separation factor R_L is defined by the equation:

$$R_L = \frac{1}{1 + K_L C_{eq}} \quad (4)$$

3. RESULTS

3.1. Adsorption Kinetics

Studies which apply adsorption isotherms demand the assessment of the adsorption coefficients at equilibrium conditions. Thereby, a previous kinetics determination has to be performed in order to establish the required time for equilibrium achievement. The adsorption kinetics results are showed in Figure 2.

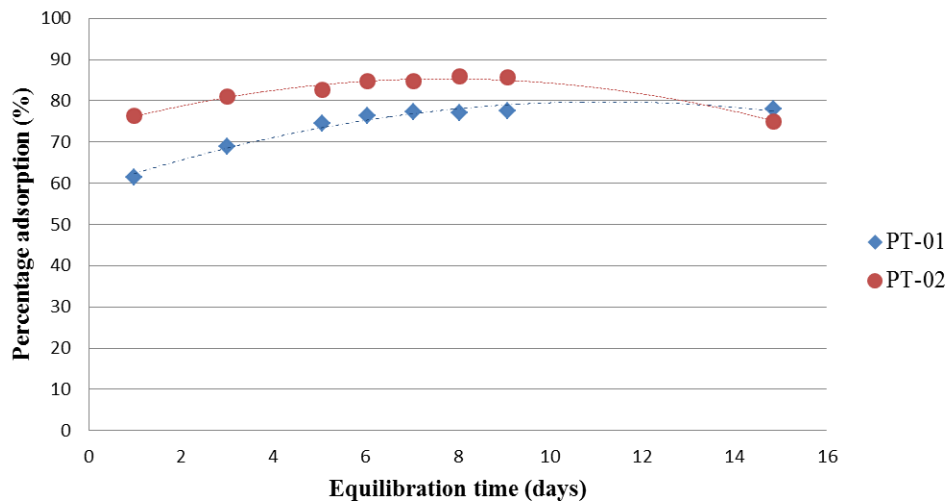


Figure 2: Percentage adsorption versus equilibration time.

As expected, cobalt adsorption on sediment was characterized by a strong affinity of the element for sediment [11]. Since around 77% of cobalt was removed from the solution by sediment PT-01, while around 88% of it was removed by PT-02, the latest was proved to be more efficient to adsolve cobalt rather than PT-01 sediment. Nevertheless, the PFB sediments are not particularly as much efficient to remove Co from seawater as other sediments reported in the literature [5].

To both sediments, adsorption equilibrium condition was reached after relatively long time, and no significant changes in the sediment adsorption percentages were observed after 6 days elapsed. As a consequence, a 8 days contact period was adopted in the isotherms experiments under same physicochemical conditions (liquid/solid ratio, pH, temperature, tracer conditions).

3.2. Desorption Experiments

Desorption experiments demonstrated that, respectively, at least 93% and 95% from the Co previously adsorbed on PT-01 and PT-02 sediments remained on the solid matrix. The desorption decreased with time and, after 8 days elapsed, only 1% and 3% of Co on PT-01 and PT-02 was desorbed, respectively, showing that cobalt adsorption on both sediments is not easily reversible (Figure 3).

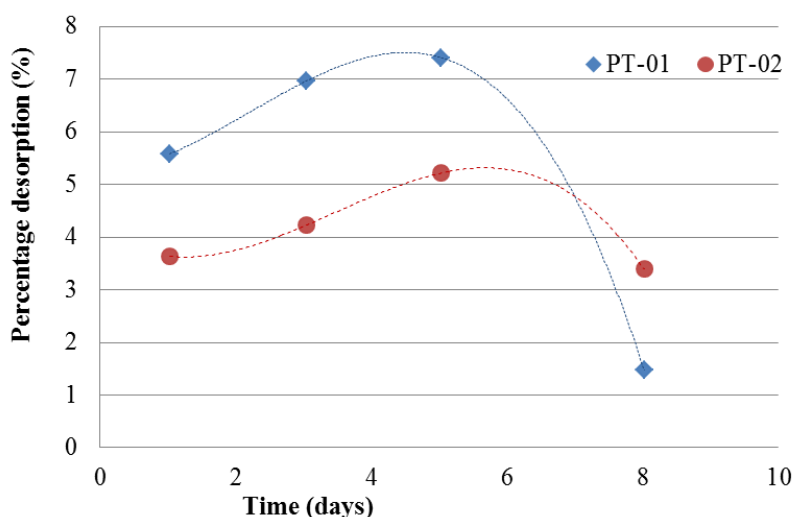


Figure 3: Desorption percentage versus equilibration time.

The desorbed ^{60}Co fraction smallness is consistent with the cobalt behavior, as described in literature [12,13] which reports that only 10% of the bound quantity can be exchanged. This irreversibility is imputed to a fixation process that occurs within the sediments and, in consequence, to the metal bonds in sites where steric access is difficult. According to BUNKER *et al.* (2000), a major cobalt fraction may be held within the Fe/Mn oxide fraction on the sediments.

The observed radionuclide decrease in solution suggests a fair released Co readsorption by the particles on the sediment with time.

3.3. Adsorptions Isotherms

Freundlich constants were determined by means of a linearized form of the Freundlich equation (figure 4). The achieved linear regression fitted to the Freundlich isotherm demonstrate that the adsorption is consistent to this model over the range of studied concentrations for both sediments, since a significant correlation does exist between the two variables (the values of correlation coefficients, R , are higher than 0.99). To both sediments, the values of $1/n$ - a fraction related to magnitude and diversity of energies associated with a particular adsorption process - are less than unity, which confirms the adsorption favorableness to both sediments. On the other hand, the $1/n$ values indicate that adsorption is slightly nonlinear for a concentration range higher than that one used in the experiments [6]. Since K_F values were much lower than 1, both sediments proved to present a rather heterogeneous surface.

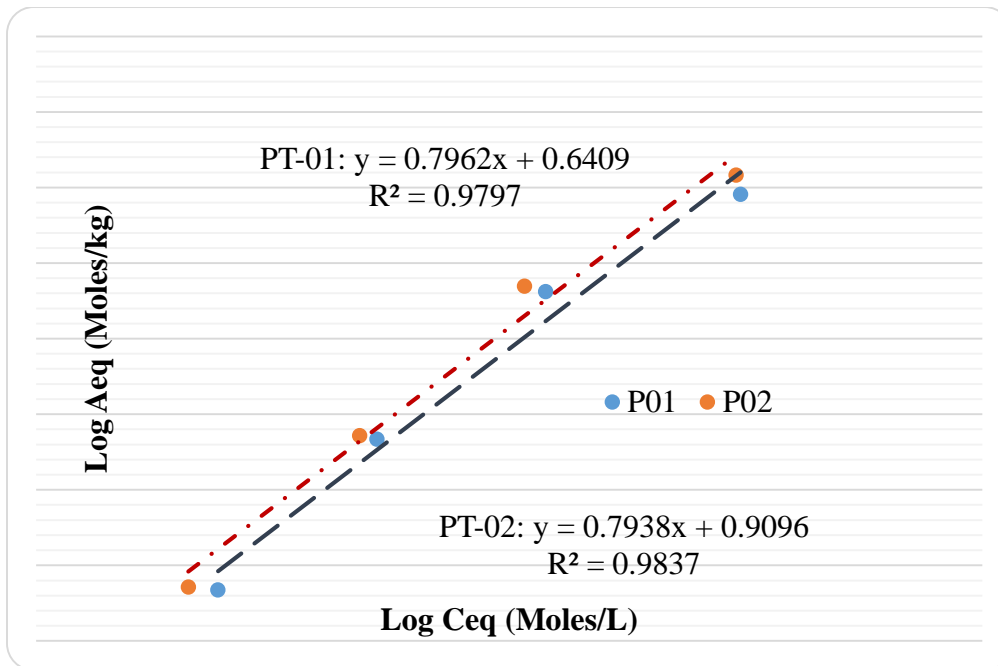


Figure 4: Linearized Freundlich adsorption isotherms.

Table 1: Determination coefficients and parameters of the adsorption isotherm

Adsorption Model	Adsorption Statistical Parameters	PT-01	PT-02
Freundlich Adsorption	R^2	0.980	0.984
	K_F (L/Kg)	4.374	8.121
	$1/n$	0.796	0.794
Langmuir Adsorption	R^2	0.999	0.999
	K_L (L/Kg)	23569	28159
	A_m (moles/Kg)	0.008	0.015
	R_L	1.000	0.034
	ΔG^0 (KJ/mol)	-24.78	-25.21

For the Langmuir isotherm, the correlation coefficient (R^2), slope and interception values were calculated by the least squares fit method, by means of the computational code ProUCL 4.1 [14]. In this case, high values of correlation coefficients were achieved, indicating a strong correlation between experimental data and Langmuir isotherm, as well as the feasibility of occurrence of Co adsorption on sediments as a monolayer adsorption.

Nevertheless, the comparisons of both isotherms and sediments produced a good accordance and correlation, with a statistical significance of 99%, which implies the feasibility of both isotherms for cobalt adsorption mechanisms studies, with the studied sediments.

The R_L parameters behavior ($0 < R_L < 1$) demonstrates the favorableness of Co adsorption on the PT-02 sediments. The maximum amount of contaminant feasible to be adsorbed on the sediments (A_m) reached 8 moles/g ($2.01 \cdot 10^{16}$ Bq/g of ^{60}Co) and 15 moles/g ($3.77 \cdot 10^{16}$ Bq/g of ^{60}Co) for PT-01 and PT-02, respectively.

From the Langmuir adsorption constant K_L , the energy of adsorption can be calculated using the following relation:

$$\Delta G^0 = -RT \ln K_L \quad (5)$$

Where:

- R is the universal gas constant ($8.3145 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$);
- T is the absolute temperature (K);
- ΔG^0 is the Gibbs free energy.

The negative values of ΔG^0 (Table 1) indicate the spontaneity of the adsorption reaction. The values are higher than the typical bonding energy for ion exchange mechanism (8-16 KJ/mol), indicating that the adsorption mechanism of cobalt ion on the sediments is not majority led by ion exchange reactions [6]. This finding is in accordance with some studies related in the literature, which identified a good association between Co and manganese oxides and suggested that some Co may become irreversible adsorbed on sediments due to its fixation on Fe/Mn oxides structures [12].

4. CONCLUSIONS

A study of Co mechanisms sorption on sediments from Piraquara de Fora Bay was performed. Regarding the sediments, results pointed out a high sorption and a small desorption. A readsorption of sediment released Co could be also observed. Both the Freundlich and Langmuir provide a good description of the data in the range of the studied concentrations and it was not possible to determine a predominant adsorption model (e.g. between monolayer or multilayer models). The adsorption process is spontaneous and favorable for both sediments. The obtained Freundlich constant (K_F) values indicate a higher heterogeneous surface in PT-01, rather than in PT-02 while ion exchange does not appear to be the most relevant binding process. Last, the maximum contaminant amounts feasible to be adsorbed on the sediments (A_m) reached 10 moles/g ($2.61 \cdot 10^{16}$ Bq/g of ^{60}Co) and 17 moles/g ($4.27 \cdot 10^{16}$ Bq/g of ^{60}Co) for PT-01 and PT-02, respectively

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