Removal of cobalt from lubricating oil by the use of bentonite: equilibrium, kinetic and adsorption preliminary studies

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ABSTRACT

Radionuclides may contaminate lubricating oils in nuclear power plants. In Brazil, this kind of waste has been stored in the generator's facilities, awaiting treatment alternatives. This work intends to investigate a process to treat it for the final deposition using bentonite as a sorbent material. Considerable volume reduction of the radioactive waste is to be attained, because the process results in decontaminated oil, free from radiological control, and radioactive loaded sorbent. The study focuses in cobalt removal from a simulated oil waste (non-active). The production of the simulated waste is described. Bentonite was used for equilibrium time determination, kinetic and adsorption studies. Cobalt adsorption equilibrium was rapidly attained after 30 minutes. The data was used for modelling the system's kinetic, applying the pseudo first and pseudo second order equation models. Experimental data fitted to pseudo second order model, supporting the assumption that the adsorption is due to chemisorption. Batch sorption tests were conducted, and the results fitted to Langmuir and Freundlich sorption models. Both isotherm models chosen for this work did not fit to the experimental data. Thus, these are preliminary results and the studies must be repeated to evaluate data variability and better statistical inference. Although, bentonite still has considerable potential as sorbent for the removal of cobalt from lubricating oil. Finally, the results might be extended to other kinds of radioactive oils and radioactive organic wastes.

Keywords: lubricating oil, bentonite sorption, cobalt, waste management.

1. INTRODUCTION

Nuclear applications in a wide range of areas such as medicine, research activities, industries and power generation produce radioactive waste. The proper management of this waste is necessary to avoid possible negative impacts on human health and the environment.

The major generators of radioactive waste are the nuclear power plants. Their operational activities generate many types of radioactive waste, among them, contaminated lubricating oil. These oils are used in many areas of a nuclear power plant and they can be easily contaminated as the oil mixes with water and other contaminants from the nuclear reactor system and becomes contaminated with radioactive waste as well as dirt and moisture [1].

Radioactive organic waste (including lubricating oils) decompose in storage and disposal and are not subject to conventional cementitious stabilization methods. Decomposition changes the chemistry of the waste, potentially degrading the stabilization material and enhancing the mobility of radionuclides and hazardous materials. In this sense, the development of new techniques of waste conditioning poses a challenge across many waste forms [2].

This kind of waste must be treated for final disposal. The most common technique used worldwide is incineration [3], as in France [4], UK [5] and Lithuania [6]. Nevertheless, Brazil does not have incinerators for radioactive waste and there is no plan to implement one in the country, due to its high costs and low public acceptance.

Wet oxidation, pyrolysis and vitrification processes have been in use since the 1990s in the nuclear industry, primarily, to volume reduction and to destroy organic wastes such as resins, oils and sludges that contain organic constituents or chelating agents [7]. These technologies are being widely tested and deployed at decommissioning of facilities in the United States and Europe. Other technologies, such as the sorption and electrochemical destruction of oils and oily wastewaters, hold promise for processing contaminated organic waste [2].

The selection of an appropriate decontamination technique for waste oil depends on the physical and chemical form of the radioactivity that is present. It is likely that radionuclides are present in one or more of the following three forms: associated with particulate matter as adsorbed ions or metallic corrosion products; dissolved in the aqueous phase of the oil/water emulsion as oxides, hydrated ions, or water soluble organics; or dissolved in the organic phase of the emulsion as organometallic complexes or other oil soluble forms [8].

Some researchers conducted studies on physicochemical treatment to remove radionuclides from oil [1] [8] [9] [10] [11]. Although they are not recent, in this work the sorption technique was chosen for its low cost and operational simplicity, desirable characteristics especially for a small inventory like the Brazilian situation. Also, the use of sorption on bentonite to decontaminate lubricating oils is a common practice for the non-radioactive ones [12] [13] [14].

Conventional physical processes can be effective in removing a large fraction of the total amount of radioactivity from waste oils, especially the filtration of particulate by and centrifugation to remove the aqueous phase associated. However, small amounts of radioactivity often remain and it is usually due to the presence of small amounts of ^{60}Co [10]. Thus, ^{60}Co would be the radionuclide more difficult to remove from the oil, especially if it is in organic soluble form.

These considerations lead to the study of oil decontamination using bentonite as sorbent for cobalt. In order to avoid unjustified exposures to radiation and radwaste generation the studies have been conducted in a simulated waste: non-active lubricating oil with organometallic cobalt incorporation.

There is extensive literature related to metal sorption on bentonite for aqueous systems, but it was not found any publication concerning adsorption and kinetic studies for cobalt in oil or organic matrix, reinforcing the relevance of this work. The aim of the present study is to remove cobalt from lubricating oil using a low-cost adsorbent bentonite. In the batch mode studies, the dynamic behavior of the adsorption was investigated at room temperature. The adsorption kinetics and Langmuir and Freundlich adsorption isotherms were also studied.

2. THEORICAL ASPECTS OF KINETIC AND ADSORPTION MODELS

2.1. Kinetic Models

The study of sorption kinetics is significant because it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. In addition, it is important to be able to predict the rate at which pollutant is removed from solutions in order to design appropriate sorption treatment plants [15].

In order to investigate the mechanism of sorption, two kinetic models have been widely used in the literature for sorption processes: pseudo-first-order and pseudo-second-order [16]–[20]. In this study, these models were investigated to find the best-fitted model for the experimental data obtained.

2.1.1. Pseudo-first-order kinetic model

This model of Lagergren assumes that the rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The equation can be rearranged to obtain a linear form showed in equation 1, where q_e (mg.g^{-1}) is the amount of sorption at equilibrium and q at time t, and k_1 is the is the pseudo-first-order rate constant for the adsorption process (min^{-1}) [15]–[17], [21].

$$\log(q_e - q) = \log q_e - \frac{k_1}{2,303} t$$

equation 1

The plot of $\log(q_e-q)$ versus t gives a straight line for first-order kinetics, which allows computation of the adsorption rate constant, k_1. When adsorption is preceded by diffusion through a boundary, the kinetics in most cases follow this pseudo-first-order rate equation. If the experimental results do not follow this equation, the sorption is not diffusion-controlled [16]. The literature data show that the equation does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption process [16], [22].

2.1.2. Pseudo-second-order kinetic model

The sorption kinetics may be described by a pseudo-second-order model. The rearranged equation to the linear form is showed in equation 2, where the rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q versus t; q_e (mg.g^{-1}) is the amount of sorption at equilibrium and q at time t [15], [23].

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$ equation 2

The pseudo-second-order rate expression has been used to describe chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces and ion exchange. In recent years, the pseudo-second-order rate expression has been widely applied to the adsorption of pollutants from aqueous solutions. The advantage of using this model is that there is no need to know the equilibrium capacity from the experiments, because it can be calculated from the model. In addition, the initial adsorption rate, h, can also be obtained from the model, represented by the term $k_2.q_e^2$ [23].

2.2. Adsorption Models

A main source of information about adsorption and its mechanism is, besides the calorimetric measurements of adsorption heat, the adsorption isotherm [24]. The relation at constant temperature between the amount adsorbed and the equilibrium pressure or concentration is known as the adsorption isotherm [25].

There are several isotherm equations available for analyzing experimental sorption equilibrium parameters, the most common being the Langmuir and Freundlich models [17], [26], [27]. The constants in the Langmuir and Freundlich equations are useful in designing adsorption process equipment [28].

2.2.1. Langmuir

The Langmuir isotherm model is based on the assumption that there is a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules [Langmuir *apud* 25].

The Langmuir model was originally proposed to describe adsorption of gas molecules onto homogeneous solid surfaces that exhibit one type of adsorption site. Many investigators have tacitly extended the Langmuir adsorption model to describe adsorption of solution species onto solid adsorbents including heterogeneous solids such as soils [29].

A well known linear form of the Langmuir equation can be expressed as equation 3, where q_e is the amount of cobalt adsorbed, C_e is the equilibrium concentration of the adsorbate and q_m and K_L are Langmuir constants related to the maximum adsorption capacity and energy of adsorption. According to equation 3, when the adsorption obeys the Langmuir equation, a plot of C_e/q_e versus C_e should be a straight line with a slope of $1/q_m$ and intercept $1/q_m.K_L$. [17], [26].

$$\frac{C}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m.K_L} \qquad\qquad \text{equation 3}$$

2.2.2. Freundlich

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centers of the adsorbent [26].

The well-known expression for the Freundlich model is given as equation 4, where q_e is the amount adsorbed at equilibrium, K_f is the Freundlich constant, $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and Ce is the equilibrium concentration.

The values of K_f and 1/n can be obtained from the slope and intercept of the plot of log q_e against log C_e [26].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \text{equation 4}$$

3. MATERIALS AND METHODS

3.1. Obtaining Simulated Waste

Brazilian Nuclear Power Plants (NPP) provided the results for the oil contamination made by gamma spectroscopy and the results show contamination with ^{60}Co and ^{137}Cs. This lead to the choice of cobalt as nuclide of interest for the simulated waste.

The two lubricating oils most used in the Brazilian NPP, Mobil Turbina 46 and Mobil SHC 624, were mixed in equal proportions. This mixture was heated until 200 °C with air injection. When the temperature was reached the standard of organometallic cobalt in mineral oil Specsol was added in a proportion to reach the final expected concentration of about 20 mg.kg^{-1}. The mix was kept at 200°C with air injection for one hour. This procedure was conducted to simulate the oil oxidation and ageing, similarly to the real contaminated oil.

3.2. Equilibrium and Kinetic Studies

The experiments were conducted in controlled room temperature of (22 ± 3) °C. The vessel was a 200 mL glass beaker with agitation by overhead stirrer. Commercial bentonite Brasgel FF (sodic smectitic activated clay) was added to samples of 100 g of simulated waste in the quantities 0.5, 1, 3, 6 and 10 g. The mixture was continuously stirred for maximum 90 min. At each predefined time, samples were withdrawn during stirring. The samples were filtered with a membrane filter of 0.45 µm to separate the loaded sorbent and the oil which was analyzed for cobalt concentration.

In order to elucidate the mechanism of sorption, two kinetic models were investigated, the pseudo-first-order kinetic model and the pseudo-second-order kinetic model.

The amount of sorption at time t, q (mg.g^{-1}), was calculated using equation 5, where C (mg.kg^{-1}) is the oil phase concentrations of cobalt at any time, C$_o$ (mg.kg^{-1}) is the initial concentration of cobalt in oil, M is the oil weight (kg) and m is the mass of bentonite (g). The tests were carried out in duplicate and q is the average value.

$$q = \frac{(C_o - C)}{m} \times M$$

equation 5

3.3. Sorption Batch Tests

The experiments were conducted at controlled room temperature of (22 ± 3) °C. The vessel was a 200 mL glass beaker with agitation by overhead stirrer. Commercial bentonite Brasgel FF (sodic smectitic activated clay) was added to samples of 100 g of simulated waste in the quantities 0.05, 0.1, 0.2, 0.5, 0.7, 1 and 3 g. The mixture was continuously stirred for 30 min as defined by the equilibrium contact time tests. After this time, they were filtered with a membrane filter of 0.45 μm to separate the loaded sorbent and the oil which was analyzed for cobalt concentration. The amount of sorption at time t, q (mg.g^{-1}), was calculated using equation 5.

Freundlich and Langmuir isotherm constants were determined from the plots of ln q$_e$ versus ln C$_e$ and C$_e$/q$_e$ versus C$_e$, using MS Excel for Windows.

3.4. Chemical Analysis

The concentration of cobalt in oil was measured by Energy Dispersive X-ray Fluorescence Spectroscopy (EDX-720, Shimadzu). Samples that showed concentrations above 0.1 mg.kg^{-1} were analyzed by atomic absorption (with air-acetilene torch, equipment AA240FS, Varian) after calcination of the oil sample and quantitative solubilization of the ashes with analytical grade HNO$_3$.

4. RESULTS AND DISCUSSION

4.1. Equilibrium and Kinetic Studies

The results are shown in Figure 1. For the S/O (sorbent/oil) ratio 0.03, 0.06 and 0.10, the equilibrium contact time was rapidly reached. For S/O ratio 0.005 and 0.01, it can be observed that the adsorption capacity increased with time and, at about 30 min, there is a tendency to reach a constant value, where no more cobalt is removed from the oil. Even though there is no complete stabilization of the amount of sorption of cobalt (q), the increments in these values are about 10^{-1} mg.g^{-1} and thus considered negligible.

Figure 1: *Equilibrium study for sorbent/oil (S/O) ratio of 0.005, 0.01, 0.03, 0.06 and 0.10.*
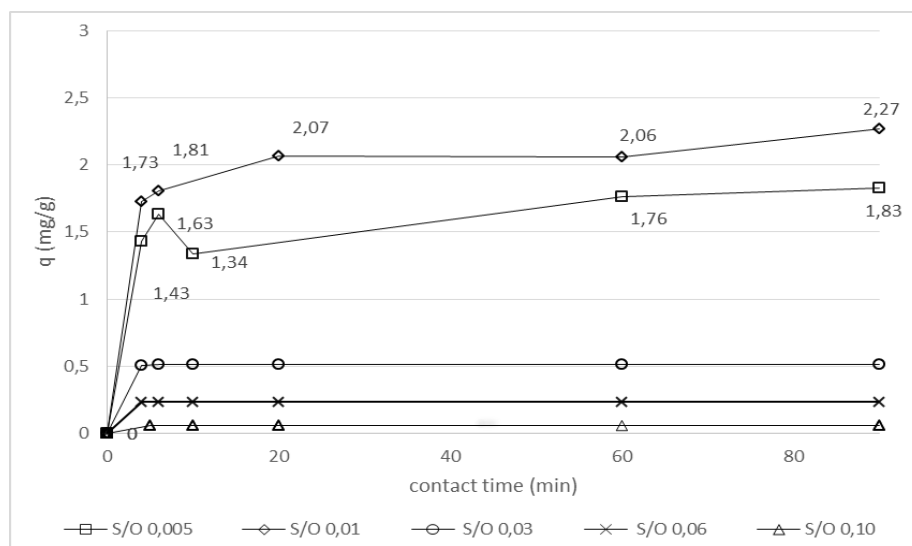
At 30 minutes, it is considered that the amount of cobalt being adsorbed onto the material is in a state of dynamic equilibrium. The time required to attain this state of equilibrium was termed the equilibrium time (t_e in min) and the amount of cobalt adsorbed at t_e reflected the maximum cobalt adsorption capacity of the adsorbent under these conditions [16]. For this reason, the equilibrium time of 30 min was assumed to be used in the following sorption tests.

For the kinetic studies pseudo-first-order and pseudo-second-order were adjusted to the experimental data of S/O 0.005 and 0.01 in order to elucidate the mechanism of sorption. Plots and linear regression were constructed using MS Excel for Windows.

Figure 2 shows the curve $\log(q_e-q)$ versus t, which should be a straight line if the pseudo first order kinetic model were applicable. The dots represent the experimental data and the line is the equation modelled. The initial q_e value was chosen as the biggest value obtained, to calculate $\log(q_e-q)$.

For the S/O 0.01 the determination coefficient, r^2, was 0.8687, and for the S/O 0.005, r^2 was 0.7823. Both r^2 are not close to 1 as expected to validate the model [30]. For this reason, parameters k_1 and q_e were not estimated. The experimental results do not follow pseudo first order model, indicating that the sorption is not diffusion controlled.

Figure 2: *Plot of log(qe−q) versus contact time t, with pseudo-first-order kinetics, for sorbent/oil (S/O) of 0.005 and 0.01.*
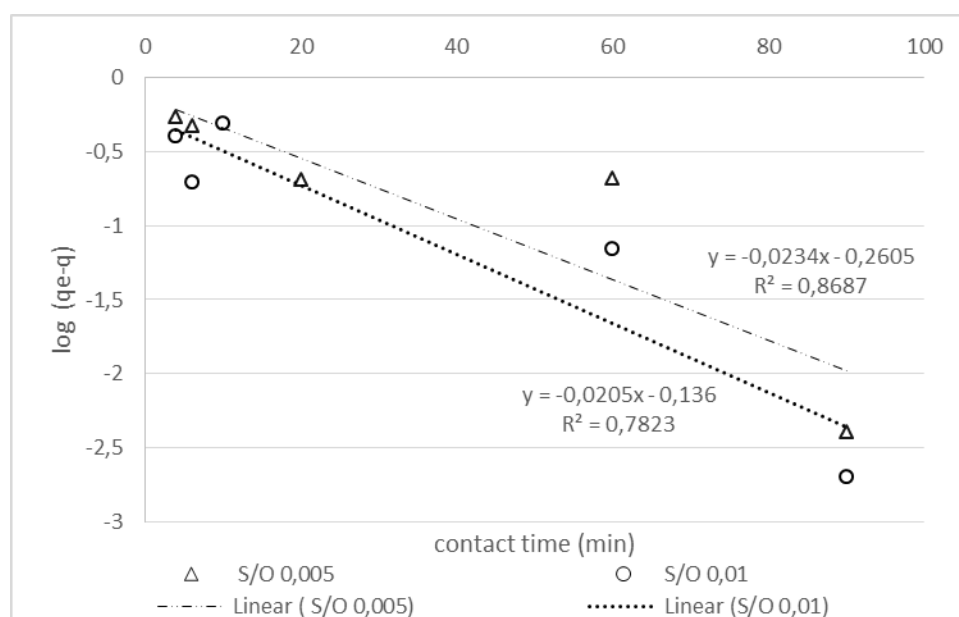
Figure 3 shows the plot of t/q versus t. The applicability of the pseudo-second-order model can be examined by considering the linearity of this plot. The dots represent the experimental data and the line is the equation modelled. For the S/O 0.01, the coefficient, r^2, is 0.9988, and for the S/O 0.005, it is 0.9966. Both r^2 are close to 1 as expected to validate the model [30]. Thus, with 95% confidence level, it can be concluded, from the plots that the pseudo-second-order kinetic model is applicable to the decontamination of oil when this bentonite is used as a sorbent.

Figure 3: *Plot of t/q versus contact time t, with pseudo-second-order kinetics, for sorbent/oil (S/O) ratio of 0.005 and 0.01.*
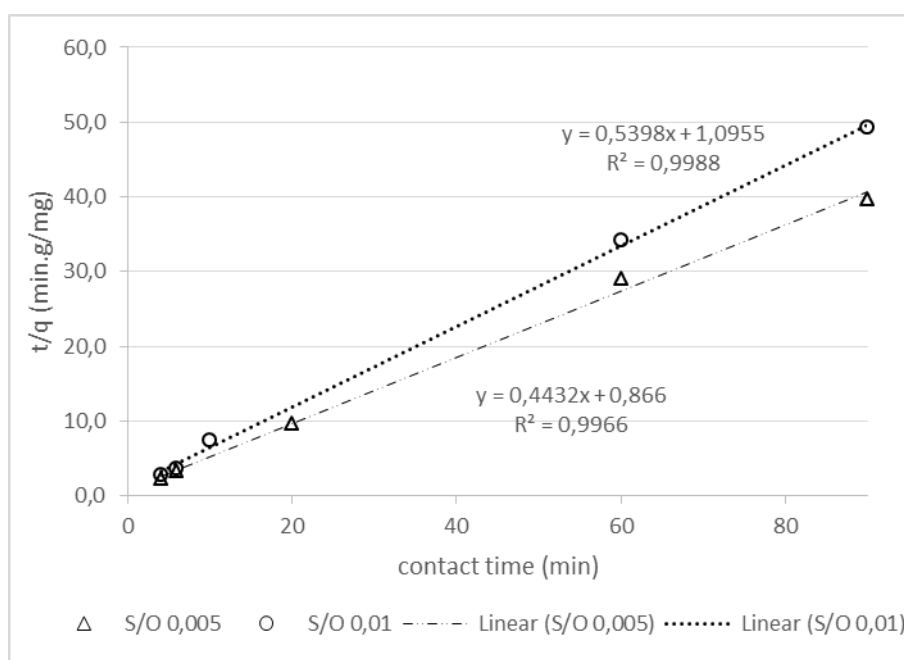

Table 1 shows the parameters determined using the linear equations of the pseudo-second order model: the coefficient, r^2; the rate constant, k_2; initial sorption rate, h; and amount of cobalt adsorbed at equilibrium, q_e (mg/g). The rate constant k_2 was expected to be the same value for both relations S/O, at the same temperature [31]. The initial sorption rate, h, is lower for the higher relation S/O, showing that the availability of sorbent does not represent higher initial sorption rate. The calculated q_e values also agree very well with the experimental data, showed at Figure 1, reinforcing

the applicability of the model. This model suggests that cobalt and sorbent initial concentrations have influence in the sorption rate.

Table 1: Linear equation for the pseudo-second order model and parameters calculated using the equation for S/O ratio 0.005 and 0.01.

S/O ratio	Linear equation	k_2 (g.mg^{-1}.min^{-1})	h (mg.g^{-1}.min^{-1})	q_e (mg.g^{-1})	r^2
0.005	t/q = 0.866 + 0.4432 t	0.23	1.2	2.3	0.9966
0.01	t/q = -0.3785 + 0.614 t	0.27	0.9	1.9	0.9988

The adsorption system obeys the pseudo-second-order kinetic model for the entire sorption period and thus supports the assumption behind the model that the adsorption is due to chemisorption. In other words, the adsorption has a character of a chemical process that occurs in a monolayer. Other kinetic models were evaluated, like Elovich and the intraparticle diffusion model [16], [18], [32], however, the coefficient r^2 for the linear equations were not close to 1.

4.2. Sorption Tests

The Langmuir and Freundlich isotherms are shown in Figure 4 and 5. The constants were determined from the plots of ln q_e versus ln C_e and C_e/q_e versus C_e, using MS Excel for Windows. Table 2 shows the linear equation obtained, the determination coefficients, r^2, for Freundlich and Langmuir models and the constants calculated for each model.

Table 2: Summary of the Freundlich and Langmuir constants, linear equation and respective determination coefficients

| Model isotherm	Langmuir	Freundlich
linear equation	$C/q_e = -2.4257/q_m + 13.305$	$\log q_e = -1.9859 + 3.7254 \log C_e$
r^2	0.5079	0.8224
Constants	$q_m = -0.41$ mg.g^{-1} $K_L = -0.18$ kg.mg^{-1}	$K_f = 0.010$ kg.g^{-1} n = 0.27

The applicability of the Langmuir isotherm to the data obtained by oil with bentonite can be examined from the plot in Figure 4. The Langmuir isotherm is well adjusted if the plot of C_e/q vs. C_e is linear. The determination coefficient calculated, $r^2 = 0.5079$, shows that Langmuir model is not applicable to the conditions studied. In addition, the calculated value for the sorption maximum amount, q_m, is unreal (even negative value) when compared to experimental data reinforcing that the model is not well fitted.

Figure 4: *Plot of Ce/q versus Ce and linear regression to Langmuir equation.*
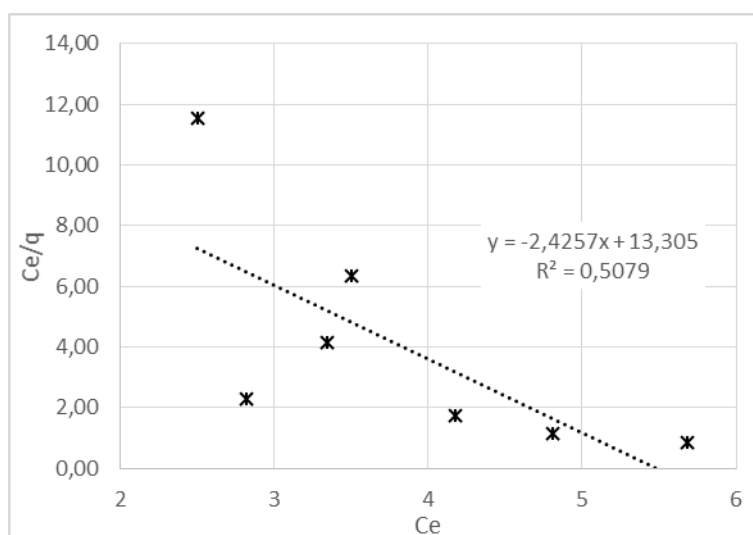
The applicability of the Freundlich isotherm to the system can be observed by considering the plots of log q vs. log C_e given in Figure 5. Generally, the linearity of the logarithmic plot is an indication that the Freundlich isotherm is being obeyed by the system under investigation. Thus, it can be concluded from the plots that the Freundlich isotherm is not applicable to the decontamination of oil when the bentonite is used as a sorbent, in the studied conditions.

Figure 5: *Plot of log qe versus Ce and linear regression to Freundlich equation.*
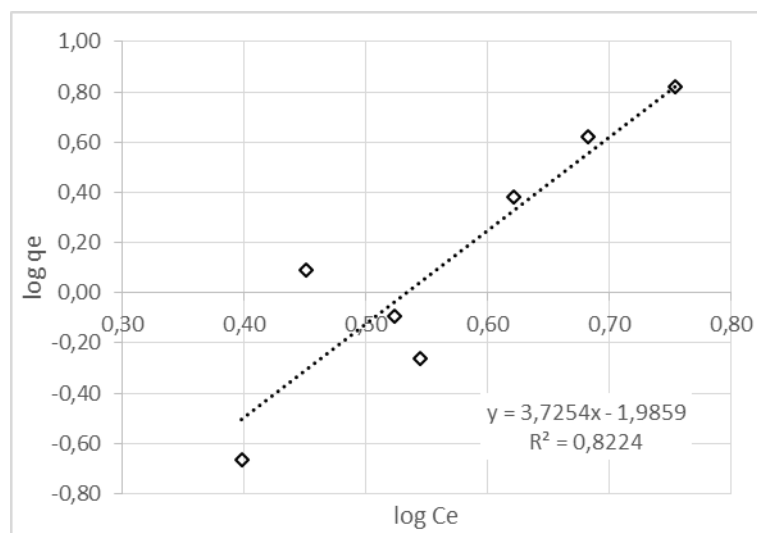
K$_f$ and n values in Table 2 were obtained from the intercept and slope in the Freundlich adsorption isotherm. K$_f$ is a constant that represents a measure of the surface area of the adsorbent [28] or an indication of the sorption capacity, whereas n can be shown to be a joint measure of the cumulative magnitude and diversity of energies associated with a particular adsorption reaction [31]. Due to the low determination coefficient and the non-applicability of Freundlich model, no conclusion can be inferred from the obtained constants.

Both isotherm models chosen for this work did not fit to the experimental data. Other isotherm models will be evaluated to choosing the best fitted one and describe the sorption of cobalt on bentonite in oil matrix.

5. CONCLUSION

It is possible to conclude that the adsorption kinetics correlated reasonably well with the pseudo-second-order kinetic model for the entire sorption period and thus supports the assumption behind the model that the sorption is due to chemisorption.

The adsorption equilibrium did not correlate with Langmuir nor Freundlich isotherm. These are the preliminary results. Further studies must be carried out for a better comprehension of the sorp-

tion mechanisms and isotherms, also applying other models and the non-linear isotherm equations now common in literature. Complete characterization of the sorbent will be done and the team is testing other sorbents. Although it was not possible to correlate the experimental data to any isotherm model tested bentonite is still considered a potential sorbent for the removal of cobalt from lubricating oil, until further studies are concluded.

6. ACKNOWLEDGMENT

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