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STUDY ON REMOVAL OF MOLYBDENUM FROM AQUEOUS SOLUTION USING SUGARCANE BAGASSE ASH AS ADSORBENT

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ABSTRACT

In the present work the adsorption ability of sugarcane bagasse ash was evaluated. The technetium-99m is a radioactive material which is used in medical diagnostic procedures. It is a decay product of molybdenum-99, which is produced mainly by the irradiation of U targets in nuclear research reactors. To separate molybdenum-99 from uranium and other fission products, adsorbents are used on the columns chromatography. In this work sugarcane bagasse was investigated as adsorbent. The sugarcane bagasse ash is a by-product of sugar and alcohol production. Adsorption ability was investigated in a batch system using molybdenum-99 as radioactive tracer. Studies of the contact time in the interval from 30 to 150 min, pH in the interval from 1 to 9 and Mo concentration from 10 $mg.L^{-1}$ to 500 $mg.L^{-1}$ were carried out. Models of Langmuir and Freundlich isotherms were used to analyze the equilibrium isotherm. The results showed that the adsorption was higher at pH 1, the equilibrium time was 120 min and the adsorption maximum capacity was 3.43 $mg.g^{-1}$. Among the isotherm models, adsorption isotherms for Mo ions by sugarcane bagasse ash were well fitted by Freundlich model.

1. INTRODUCTION

The ever increasing demand for radioisotopes for medical applications received worldwide attention in 2009 owing to the serious shortages faced in the supplies of medical isotopes, especially fission molybdenum-99 [1].

The 99Mo is produced by the fission of 235U targets (99Mo fission yield 6.1%) in nuclear research reactors. The irradiated targets are then processed and the resulting purified 99Mo solution subsequently distributed for use in the production of 99Mo–99mTc generators [1].

Over 80% of diagnostic nuclear medical imaging uses radiopharmaceuticals containing technetium-99m (99mTc), entailing over 30 million investigations per year. The excellent nuclear characteristics of 99mTc enable high quality images with low radiation doses to patients. Its chemical characteristics make it very versatile for attaching to different chemical substances, so that it can be used to target different organs and diseases as required by different diagnostic procedures [1].

Purity requirements for 99Mo are very high, and extensive quality controls are essential [1]. To separate molybdenum from uranium and other fission products adsorbents are used, usually commercial resins.

In this work the sugar cane bagasse ash was used as an alternative adsorbent to retain molybdenum in one of the purification process steps.

Sugar cane bagasse corresponds to 20-25% of the weight of the sugarcane processed. According to the Ministry of Agriculture, Livestock and Food Supply of Brazil the annual production estimated in 2010 was 574.580.250 ton. It is produced in almost all over the country and only the state of São Paulo produces 60% of the total [2].

It is a residue from the sugar-alcohol industry and can be used to produce electric power through cogeneration. Cogeneration is the process of transforming a given form of energy into more than one form of useful energy. The more common types of cogeneration are: mechanical (to drive machinery, equipment and electric power generation turbines) and thermal (for the generation of steam, cold, or heat) [3]. If the cogeneration is thermal the sugar cane bagasse is burned in broilers to produce steam and its by-product is the sugarcane bagasse ash [3].

Sugarcane bagasse ash has been used to produce ceramic materials [4] and in this study it was used as adsorbent.

2. MATERIAL AND METHODS

The sugarcane bagasse ash was collected from the bottom of a broiler in an alcohol factory at Junqueirópolis, São Paulo, Brazil. It was not submitted to pretreatment.

The radioactive tracer of molybdenum-99 was used in these experiments. The method consists of adding small amounts of radioactive material into the solution of Mo carrier. The radioactive material presents the same chemical behavior of non-radioactive molybdenum, therefore it is possible to determine its concentration. It was chosen because it is a fast method of analysis and provides reliable results. The 99Mo tracer was supplied by the Radiopharmacy Centre –RC/IPEN.

The initial molybdenum solution consisted of non-radioactive molybdenum in different concentrations containing the molybdenum radioactive tracer (3 µL) and different pH values adjusted by the addition of drops of aqueous HCl or NaOH solutions.

2.1. Batch Adsorption

The adsorption of molybdenum on the sugarcane bagasse ash was investigated in a batch system. All batches were conducted at 25 ± 2°C, performed in duplicate at least and the mean values were presented.

The molybdenum solutions (1.5 mL) were in contact with the sugarcane bagasse ash (50 mg) in glass bottles at different time intervals under agitation at 200 rpm. The supernatant solution was filtered through Whatman filter paper to separate the solid and liquid phases. The initial solution, which was not in contact with the adsorbent, was also filtered.

The activity of molybdenum radioactive tracer of the supernatant solution was counted by a gamma ray spectrometer of Hyperpure germanium detector (HPGe) (Canberra) before and after contact with the adsorbent.

Figure 1 illustrates the flow sheet of the experimental procedure.

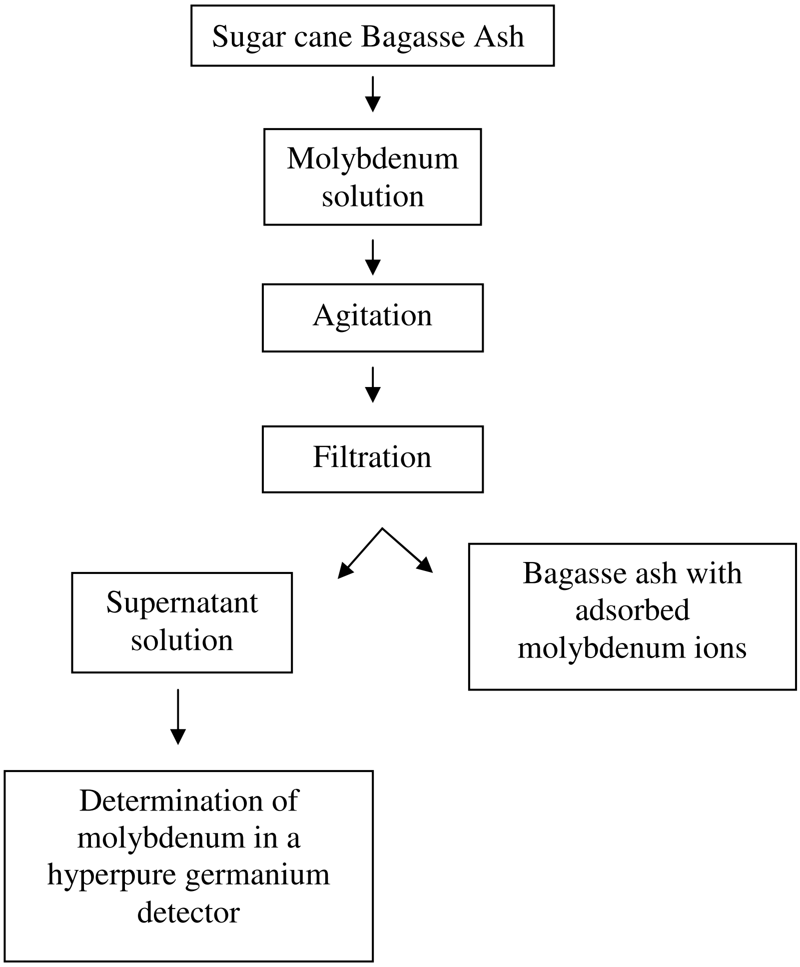

Figure 1. Flow sheet of the study of molybdenum adsorption on the bagasse ash by the batch system.

The removal percentage (% removal) was monitored by analyzing the molybdenum concentration before and after contact with sugarcane bagasse ash. The % removal was calculated from the Equation 1.

$$\% \text{ removal} = (C_i - C_f) / C_i * 100 \quad (1)$$

where C_i and C_f are the initial and final molybdenum concentration in the aqueous phase, before and after the contact of the aqueous phase with the adsorbent phase [5], respectively.

2.2. Effect of pH on adsorption

The dependence of metal ions removal with pH is related to both surface functional groups present on the adsorbent and the metal ion form in solution [6].

The influence of pH on adsorption was investigated at 1, 3 and 9 pH values. Fifty milligrams of sugarcane bagasse were in contact with 1.5 mL of 0.48 mg L^{-1} of molybdenum solution. The contact time was 60 min. The pH value was measured using a pH meter at the beginning of the experiments and not controlled afterwards.

2.3. Effect of Contact Time

The experiments were conducted to quantify the effect of contact time on the molybdenum sorption. The contact time interval was from 30 to 150 min, the solution pH was 1 and the molybdenum concentration was 0.48 mg L^{-1}.

2.4. Adsorption Equilibrium Isotherm of Mo on the Sugarcane Bagasse Ash

Adsorption equilibrium isotherm describes the interaction behavior between the different concentrations of adsorbates and the adsorbent by the adsorption on the equilibrium. Molybdenum solutions (1.5 mL) with concentrations varying from 10 to 500 mg L^{-1}, pH 1, were contacted with 50 mg of sugarcane bagasse ash during 120 min for determining the sorption capacity of the sugar cane bagasse ash for molybdenum. The data were evaluated by adsorption isotherm models of Langmuir and Freundlich to describe the adsorption data.

Langmuir isotherm model assumes monolayer adsorption, and is presented by the Equations 2 and 3.

Langmuir model in nonlinear form $q_{eq} = Q_{max}*K_L*C_{eq} / (1+K_L*C_{eq})$ (2)

Langmuir model in linear form $C_{eq}/q_{eq} = 1 / (Q_{max}*K_L) + 1 / Q_{max}*C_{eq}$ (3)

Where q_{eq} is the amount adsorbed (mg g^{-1}), C_{eq} is the equilibrium concentration of adsorbate in the solution (mg L^{-1}), Q_{max} is the maximum adsorption capacity (mg g^{-1}), and K_L is the constant related to the free energy of adsorption.

The Freundlich model is presented by the Equations 4 and 5.

Freundlich model in nonlinear form $q_{eq} = K_F *C_{eq}^{1/n}$ (4)

Freundlich model in linear form $\log q_{eq} = \log K_F + 1/n *\log C_{eq}$ (5)

where C_{eq} is the equilibrium concentration (mg L^{-1}), q_{eq} is the amount adsorbed (mg g^{-1}), K_F is a parameter of relative adsorption capacity of the adsorbent related to the temperature and *n* is a characteristic constant for the adsorption system [5].

3. RESULTS AND DISCUSSION

3.1. Effect of pH on adsorption

The results of the influence of pH on adsorption are presented in Figure 2.

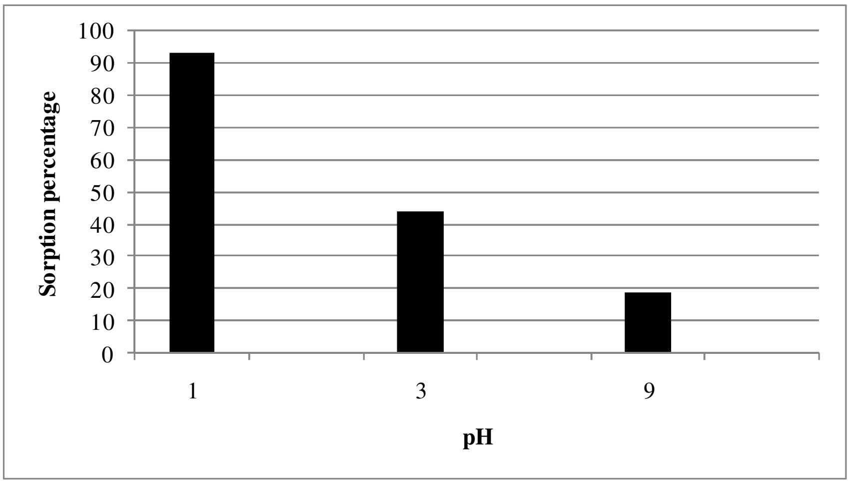

Figure 2. Influence of pH on the molybdenum adsorption by the sugarcane bagasse ash

Figure 2 shows that the adsorption of molybdenum (%) decreases when pH value increases. The Mo adsorption on the sugarcane bagasse ash is very favorable at acid pH, however at basic pH, the adsorption is low. The maximum adsorption efficiency was 92.95% at pH 1 and this pH value was selected as optimum pH for further studies.

3.2. Effect of Contact Time

Figure 3 shows the percentage of adsorbed molybdenum on the sugarcane bagasse ash in different contact times.

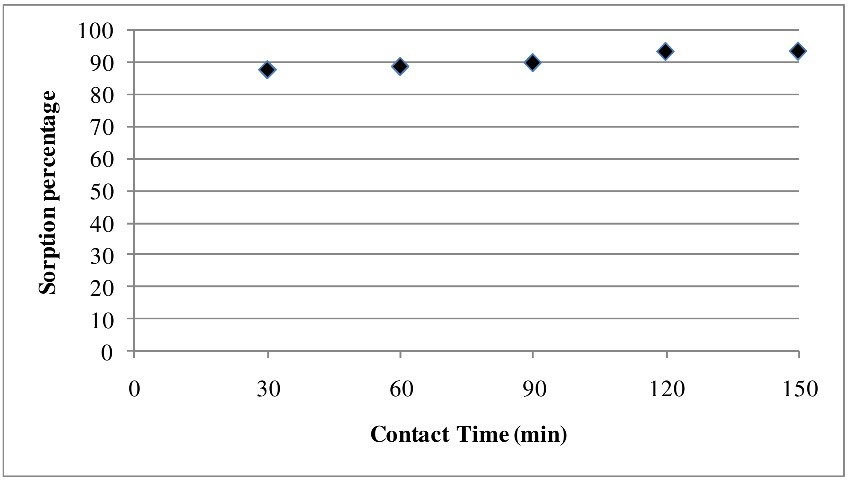

Figure 3. Effect of contact time on the molybdenum adsorption by the sugarcane bagasse ash

The adsorption increases with the increasing of contact time until it reaches the adsorption equilibrium, which was at 120 min. From this time, the adsorbed Mo by sugarcane bagasse ash is in equilibrium with the Mo concentration in the solution. Therefore the adsorption equilibrium isotherm was obtained with 120 min of agitation.

3.3. Adsorption Equilibrium Isotherm of Mo on the Sugarcane Bagasse Ash

To evaluate the adsorptive capacity of sugarcane bagasse ash for Mo ions from the solution of pH 1, the Freundlich and Langmuir adsorption isotherm models were fitted.

Figure 4 and Figure 5 represent the plot of the experimental data based on Langmuir and Freundlich isotherm models, respectively.

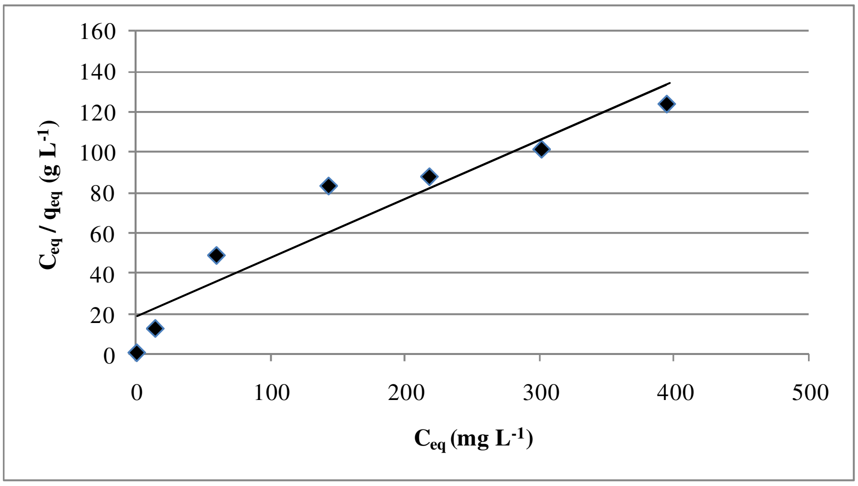

Fig. 4. Langmuir isotherm model (linear) adjusted for the molybdenum adsorption isotherm on the sugarcane bagasse ash

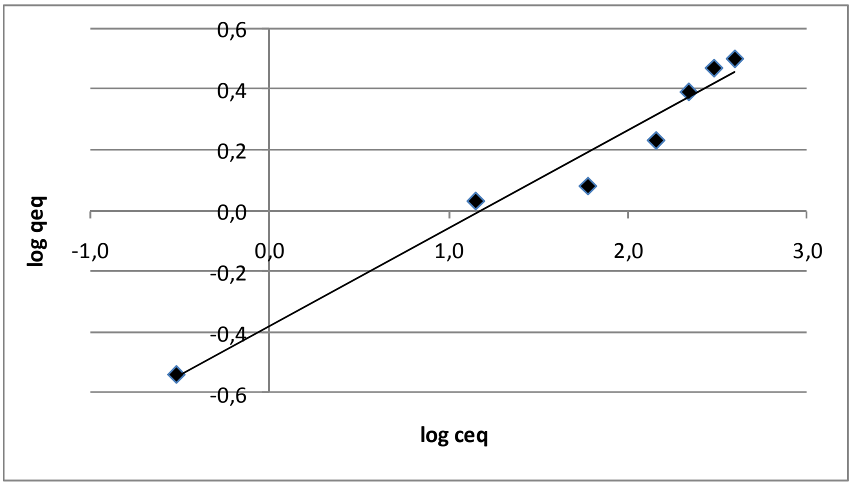

Fig. 5. Freundlich isotherm model (linear) adjusted for the molybdenum adsorption isotherm on the sugarcane bagasse ash.

Parameter values of the Langmuir and Freundlich isotherm models for the Mo ions on the sugarcane bagasse ash are presented in Table 1.

Table 1. Parameter values of the Langmuir and Freundlich isotherm models for the molybdenum ions on the sugarcane bagasse ash

Isoterm Model	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	1/*n*	K_F	r^2
Langmuir	3.43	0.015	-------	-------	0.900
Freundlich	-------	-------	0.322	0.414	0.967

Figure 6 compares the predicted data by the Langmuir and Freundlich isotherm models for system with the experimental isotherm.

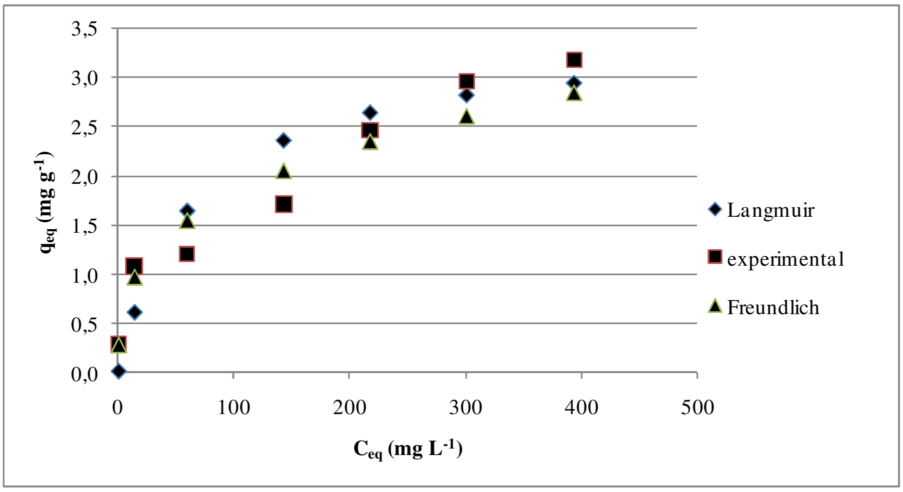

Figure 6. Comparison between the experimental isotherm of the Mo ions on the sugarcane bagasse ash and the isotherm models.

Figure 6 shows that both Langmuir and Freundlich model fitted the adsorption equilibrium isotherm of Mo ions well. However the Freundlich linear model was fitted with a greater value of coefficient correlation (r) and it was closer to unity (0.967) indicating that the Freundlich model describes the Mo isotherm better than the Langmuir linear model. The adsorption capacity of the sugarcane bagasse ash for molybdenum, established by Langmuir model, was 3.43 mg.g^{-1}.

4. CONCLUSION

The study showed that the sugarcane bagasse ash can adsorb > 92% of the Mo ions from the acid medium, pH 1. The adsorption isotherm was best described by the Freundlich model and the adsorption capacity established by Langmuir model was 3.43 mg.g^{-1}. The sugarcane bagasse ash is an alternative material to the high cost adsorbents for Mo ions purification and has a great potential of application for separation process of the fission 99Mo. For further studies, the molybdenum desorption, ash dosage, influence of metal ions, such as Te, Ru and Iodine and columns chromatography will be investigated.

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