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# Using the response surface methodology (RSM) to plan adsorption tests

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## Abstract

Chemical contamination of water can occur both naturally (geogenically) and through anthropogenic activities, and many of these contaminants are resistant to biological degradation methods or cannot be effectively removed through physical-chemical treatments. About the fluoride ($F^-$), geogenic sources for natural waters include volcanic products, igneous rocks and clay minerals, or anthropogenic sources through mineral processing and mineral coal consumption. Exposure of humans to high concentrations of fluoride can cause health problems such as fluorosis, osteoporosis and problems with organs such as the lungs, nerves and kidneys. Adsorption is a technique that has received a lot of attention because it is easy to operate, requires limited space, is environmentally friendly and is the most economical way of removing species present at low levels. The objective was to find the optimum point with the lowest temperature and highest fluoride ion removal rate and yield in biochar production. For the tests, biochar was produced with a flow of $N_2$ by varying the reaction time and temperature, using a central composite design with two factors and three levels ($3^2$). Using the R software, the response surfaces and contour levels were determined to determine the optimum points for the greatest efficiency in fluoride removal and the greatest yield in the production of biochar using waste coffee ground. The use of the response surface method (RSM) showed promise in planning the production of alternative coals.

*Keywords:* biochar; fluorite; adsorption; SRM

## 1. Introduction

The chemical contamination of water by a wide range of organic and inorganic pollutants, such as toxic metals, BTEX (group of compounds made up of hydrocarbons: benzene, toluene, ethylbenzene and xylenes), HPA's (Polycyclic Aromatic Hydrocarbons), anions, among other pollutants, has triggered the need to develop technologies to remove these pollutants found in liquid and gaseous waste. These substances, found in trace quantities, generally resist biological degradation methods or are not effectively removed by physical-chemical treatment methods [1].

Sources of contamination can occur from geogenic (or natural) sources, including volcanic products, igneous rocks and clay minerals, where the chemical weathering of these minerals releases fluoride into the biota, atmosphere, dust, soil and water, and from anthropogenic sources [2] [3]. Anthropogenic sources of fluoride to natural waters include the use of phosphate fertilizers, the manufacture of glass and the burning of mineral coal [4].

Exposure of humans to high concentrations of fluoride, caused by effluent pollution resulting from local industrial activities, can lead to health problems such as dental and skeletal fluorosis, osteoporosis and problems in organs such as the lungs, nerves and kidneys [5]. It is therefore necessary to reduce the concentration of $F^-$ in drinking water to bring it within the permitted levels.

Various methods are used to remove fluoride from water and industrial effluents, such as adsorption, coagulation, filtration, chemical precipitation and reverse osmosis. Among these, the most used method is adsorption. Adsorption is a physical-chemical phenomenon in which elements accumulated and concentrated in the liquid or gaseous phase are transferred to solid surfaces. The removal of molecules, ions or chemical species from the surface is called desorption [6].

Adsorption separation methods are basically based on three different mechanisms: steric, equilibrium and kinetic. In the steric mode, the pores of the adsorbent material have characteristic dimensions, which allow certain molecules to enter, excluding the others. For equilibrium mechanisms, different solids are assigned to accommodate different types of adsorbates, which are adsorbed preferentially to other compounds. The kinetic is based on the different diffusivities of the various species in the adsorbent pores [1].

Adsorption is one of the techniques that has received a lot of attention because it is an easy operation, requires limited space, is environmentally friendly and the most economical [7].

## 2. Objective

Find the optimum point with the lowest temperature and highest fluoride ion removal rate and yield in biochar production

## 3. Methodology

Samples of waste coffee grounds were collected from local businesses, homogenized, dried in an oven at 105ºC for 24 hours and stored under refrigeration in airtight bottles. Subsequently, 50 grams fractions of this material were pyrolyzed with a flow of $N_2$ (200mL.min$^{-1}$) in a ceramic reactor inside a SANCHIS tube furnace with variations in pyrolysis reaction time (x1) 120, 180 and 240 min (-1, 0, +1) and temperature (x2) 400, 500 and 600 °C (-1, 0, +1).

The pyrolyzed samples were washed with reverse osmosis water at room temperature until no caffeine was found in the wash water. The charcoal was then dried in an oven at 105ºC for 24 hours and stored. The adsorption tests were carried out by placing 0.1 g of each activated carbon in contact with 50 mL of a solution of 10 mg. L$^{-1}$ solution of fluoride ions in 125 mL erlenmeyers flasks under continuous stirring at 200 rpm and 25 °C. The concentration of $F^-$ was estimated using a Fluorimeter (550 Analyzer).

The results obtained were statistically analyzed using R software, using the response surface analysis methodology with a 3² factorial central composite design.

## 4. Results and discussion

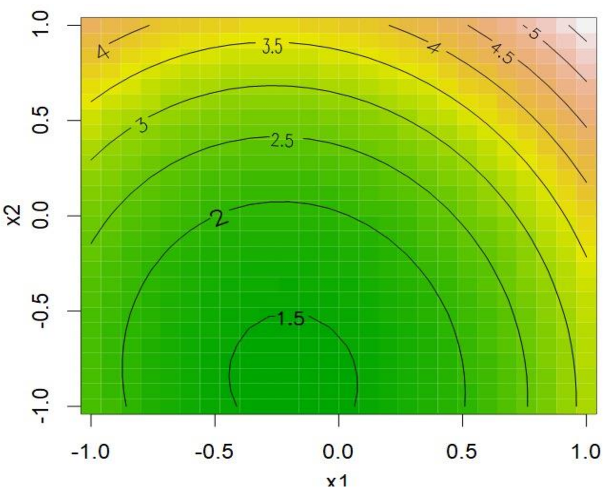
In the tests, was obtained: the yield (%) obtained after pyrolysis (y) and the removal rate (%) of $F^-$ (z).

Table 1 - Results obtained for $F^-$ removal and biochar production yield.

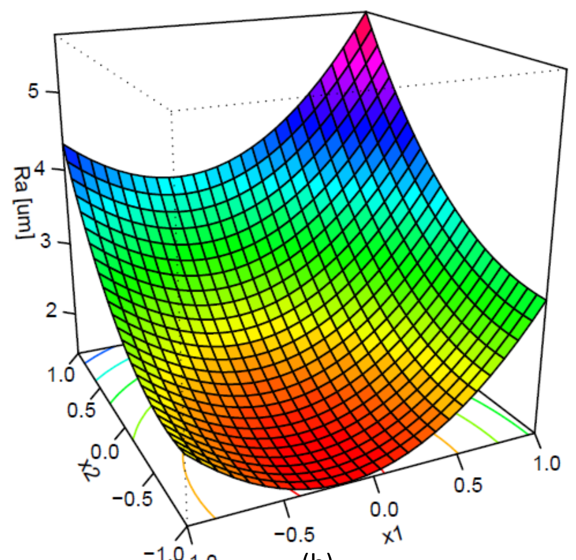
| # | x1 | x2 | y | z |
|---|---|---|---|---|
| **1** | -1 | -1 | 28.563 | 2.04 |
| **2** | 0 | -1 | 29.248 | 1.21 |
| **3** | 1 | -1 | 30.115 | 3.59 |
| **4** | -1 | 0 | 25.356 | 2.74 |
| **5** | 0 | 0 | 26.306 | 3.16 |
| **6** | 1 | 0 | 25.145 | 2.46 |
| **7** | -1 | 1 | 25.329 | 4.46 |
| **8** | 0 | 1 | 24.455 | 2.88 |
| **9** | 1 | 1 | 23.424 | 6.53 |

Applying the data obtained to the R software, the graphs in figure 1 were obtained, where it was observed that there was a trend towards greater fluoride removal at higher temperatures in pyrolysis conditions of 600ºC and 240 min. Looking at the contour graph, the tendency for adsorption to increase starts at the points with time at 120 min and 600ºC with curves above 4% removal efficiency.

Figure 1 - Contour plot (a) and surface in relation to $F^-$ removal efficiency (b)




(a)



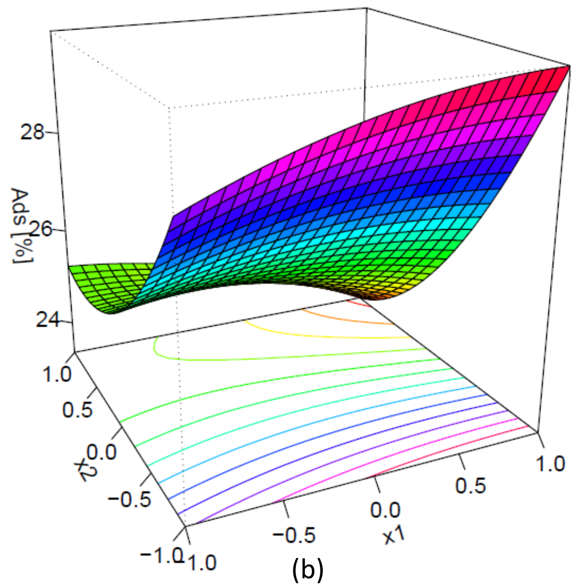
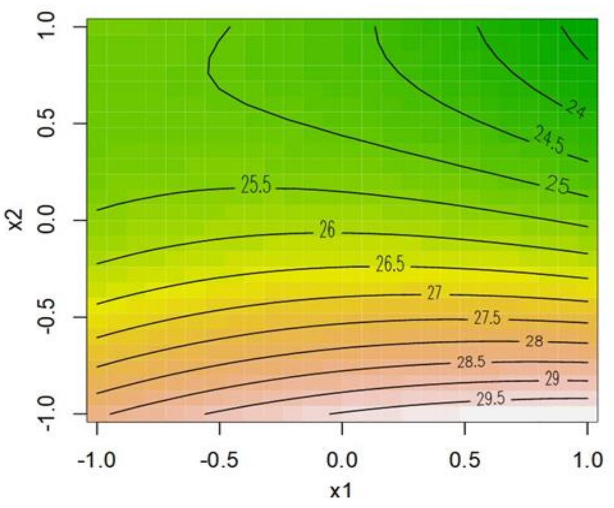




Figure 2 - Contour graph (a) and surface in relation to charcoal production yield (b)

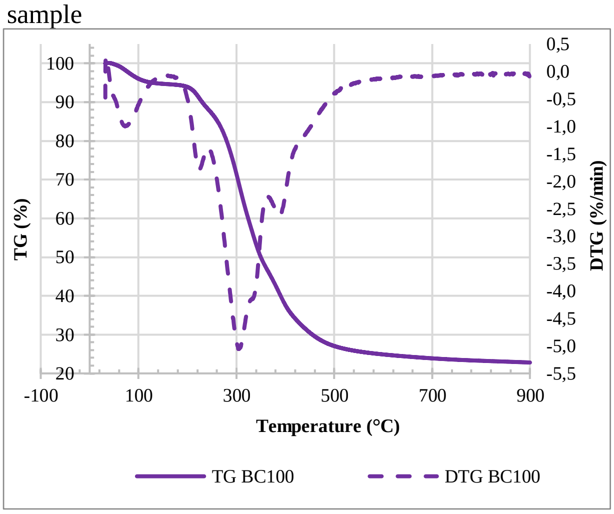



The figure 2 shows a trend towards better charcoal production yields at temperatures in the region of 600ºC for 2 hours of pyrolysis reaction. The results found, in turn, may be linked to the optimization of the sample preparation process and the use of the pyrolysis system.

Therefore, since the reaction time is directly linked to energy consumption, the choice of producing biochar from waste coffee grounds is more viable for subsequent activation at 600ºC for 120 min in this study.

Another point to consider is the thermogravimetric analysis of the material to be processed. According to Figure 3, from the temperature of 500ºC there is a tendency towards stability in the mass loss of waste coffee grounds, but the feasibility of producing charcoal at high temperatures must be considered due to technical and operational limitations.

Figure 3 - TG/DTG curve of the waste coffee grounds sample




(b)

## 5. Conclusion

The use of statistical methods through the R software is an important tool for decision-making in the experimental planning of the study to obtain alternative coals for future developments of activated coals.

Considering the results obtained, the optimum point for F- removal and a higher yield in charcoal production is 600ºC for 120 min. The shorter time has no influence on compensating for the greater energy expenditure to be incurred with double the time at a higher temperature and a gain in adsorption performance. As it is an easily accessible waste product, the use of a larger quantity of adsorbent can be used to compensate for its removal.

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