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RESEARCH ARTICLE

OPTIMIZATION OF COPPER IONS ADSORPTIVE PROCESS ON DRILLING CUTTING ASH (DCA) FROM RESPONSE SURFACE METHODOLOGY (RSM)

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ABSTRACT

Produced Water (PW) and drilling gravel are tailings from the oil industry, and their management and treatment represent a key challenge for the oil industry. The literature reports numerous physicochemical techniques for the treatment of PW, and the adsorption process is the most attractive when removing traces of toxic metals present in this effluent, mainly due to its low cost, high selectivity and fast adsorption kinetics. The objective of this work was to optimize the adsorption process of bivalent copper ions in aqueous medium in the drilling cutting ash (DCA) from the surface response methodology. Adsorption assays were conducted in batch, under parameters (Adsorbent Mass, Initial Adsorbate Concentration) and predetermined operating conditions (stirring speed, temperature, pH, contact time and volume of synthetic solution). Based on the results of removal efficiency (87 to 100%) and adsorption capacity (divalent copper), a factorial design was performed using Statistica 7.0 software, evaluating the interaction of the adsorptive process parameters and their effects on the obtained results. And from the response surfaces for each parameter, it can be observed that for any DCA mass range (g) high levels of removal efficiency of bivalent copper ions were obtained, as well as high adsorption capacity for these metals. The results show that drilling cutting ash becomes a promising material for use in adsorptive processes in the treatment of produced water from oil fields.

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INTRODUCTION

During oil exploration and production, various wastes are generated, such as produced water (PW) and drilling cutting (DC). Produced water is an effluent of complex chemical composition, since it has organic compounds, salts and toxic metals, among other contaminants, making it the treatment and final destination of this effluent a challenge for the petroleum sector. The literature reports that the total volume of PW generated reaches values above 39 million cubic meters per

day which definitely represents a key challenge to find alternative methodologies for treatment of this pollutant. Already drilling cutting is a waste obtained during the drilling phase of oil wells, which must be treated and disposed of properly, given that hydrocarbons and soluble salts are present, and these can cause serious damage to nature and human health (Al-Ghouti, 2019). In Brazil, the reuse and disposal of PA are regulated by CONAMA following resolution 430/2011 (Ministério do Meio Ambiente, 2005), which provides for the conditions of concentration of contaminants in the effluent, and for copper ions a limit of up to 1ppm is established. The treatment of PW by adsorptive processes has been reported in the literature as an alternative and promising method, because

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the process presents high selectivity, low cost and high removal efficiency of several contaminants. In parallel, the criteria for developing new adsorbents to be applied in wastewater treatment involves some factors such as adsorption capacity, recycling, high porosity, surface area, active sites and cost to obtain (Fard, 2016). Given this, this residue obtained during well drilling is not as explored in the literature as its application in adsorptive processes. However the ashes obtained from this tailings can make it an attractive adsorbent material for the removal of traces of toxic metals (copper, zinc, cadmium, lead, among others) present in water produced from oil fields.

Objective: Optimize adsorption process of copper ions on ashes of drilling cutting from the response surface methodology (RSM).

MATERIALS AND METHODS

Synthesis of adsorbent: The drilling cuttings (DCs) were triturated in a food processor and calcined at temperature 500 °C in a muffle (model 305C, Shimadzu) furnace for 2 hour.

Distribution of particle of drilling cutting ash (DCA): The relative distribution the particles of DCAs were determinat utilization from a set mesh sieves of pre-determined openings (600 to 75 µm), under mechanical agitation for 10 minutes.

Composition chemical of adsorbent: The analysis chemical composition the DCA were determined by X-ray fluorescence, utilization spectrometer type Axios Max of Panalytical.

Calibration curve and stability the ions of copper in middle aqueous: A synthetic solution using copper sulfate (CuSO₄) was prepared in the laboratory to determine bivalent copper ion concentration in aqueous medium. A calibration curve was constructed from the absorbance as a function of copper ion concentrations (250 to 5000 mg. L⁻¹) at the maximum absorption wavelength (λ_{max}), following Lambert-Beer law using one spectrophotometer (SHIMADZU UV-201) UV-visible. In parallel stability of the synthetic solution produced front of external factors, such as light, atmospheric air, humidity and temperature, so order to quantify the change in absorbance over time (75 min).

Sorption studies: The assays were conducted in batch, under agitation, temperature, volume and constant pH (300 rpm, 25 °C and 6.0, respectively), varying the initial concentration of adsorb ate (1.0 the 5.0 g.L⁻¹) and mass of adsorbent (0.2 the 1.0 g). The adsorption capacity (q_e) of ions Cu²⁺ to DCA (mg.g⁻¹) was calculated using the following Equation 1⁵.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Herein, C₀ and were the initial and equilibrium Cu²⁺ concentrations (mg.L⁻¹); V was the volume (L) of the Cu²⁺ solution and m was the mass of DCA (g). From the data of C₀ and C_e, fromed possible to determine the removal efficiency (RE) of Cu²⁺ by the presence of DCA in the adsorptive process, from Equation 2.

$$RE(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Response surface methodology (RSM): The factorial plannig (3²) can applied, utilizatio from the Statistica 7.0 software with the following input variables and output, under coded conditions and actual values according to Table 1. Based on Table 1, it was possible to obtain a mathematical model that quantifies and compares the effects that the variables X₁ and X₂ exert on the output variables (removal efficiency and adsorption capacity).

RESULTS AN DISCUSSION

Distribution of particle of drilling cutting ash (DCA): The average size distribution of the selected particles were 75 µm. This parameter is fundamental for liquid-solid adsorptive processes, due to obtaining a larger surface area, which favors the adsorption of the contaminant on the solid surface (adsorbent). For adsorptive processes the uniform distribution and particle size reduction influence the increase in the surface area of the adsorbent material, and consequently in the adsorption process, since it is a surface phenomenon. For larger particles, the diffusion resistance is lower and much of the inner surface of the particle is not available for adsorption (Sekar, 2004).

Chemical composition of adsorbent: Table 2 shows the chemical composition obtained in the FRX assay for sample the drilling cutting ash (DCA). Table 2 it is evident the predominance of silica (SiO₂) present in the sample. This fact will corroborate the process of adsorption of copper ions present in aqueous medium, since silica hydrolysis will produce silanol group (SiOH), by the cationic reaction between metallic and hydroxyl ions (Vimal Chandra Srivastava, 2006).

Calibration curve and stability the ions of copper in middle aqueous: Graph 1 represents the calibration curve of Cu²⁺ solutions from the absorbance reading of the aliquots of each solution for a wavelength of 775 nm. From graph 1 it can be observed that the regression coefficient obtained is close to 1 (R² = 0.99), which can transform the straight line equation the straight to quantify equilibrium concentration of copper ions (C_e) in the adsorption tests as a function of absorbance (Abs), according to Equation 3.

$$C_e = \frac{Abs - 0,005}{0,0001} \quad (3)$$

Graph 2 represents the stability of the synthetic solution produced front of external factors over time. Graph 2 shows that there is no change in absorbance, that is, remained stable, which definitely indicates that any change in absorbance is due to the presence of the adsorbent used in the adsorption tests.

Response surface methodology (RSM): Based on the results obtained in the adsorption tests (See Table 1) and the factorial design applied with Statistica software, it was possible to obtain the mathematical models (Equations 4 and 5).

$$RE(\%) = 75,13 + 45,10 \times DCA\ mass - 20,21 \times (DCA\ mass)^2 + 0,005 \times C_0 - 2,86 \times 10^{-7} \times C_0^2 - 0,004 \times DCA\ mass \times C_0$$

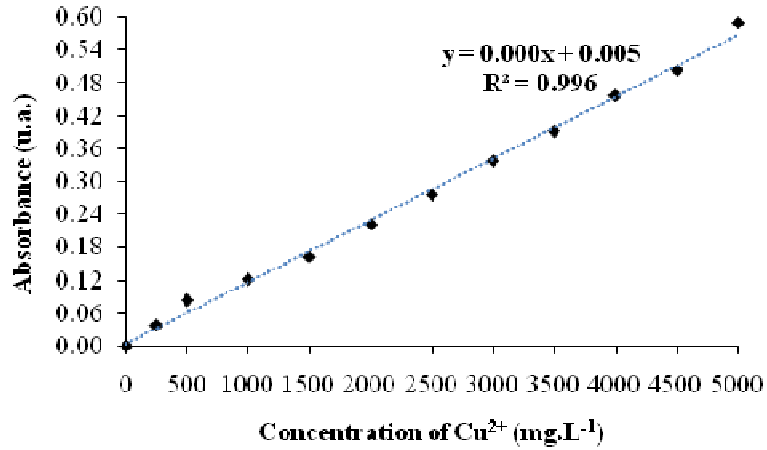
$$q_e\ (mg/g) = 150,50 - 798,13 \times DCA\ mass + 690,94 \times (DCA\ mass)^2 + 0,17 \times C_0 + 3,05 \times 10^{-7} \times C_0^2 - 0,15 \times DCA\ mass \times C_0 \quad (5)$$

Equations 4 and 5 allowed to calculate the prediction of Removal Efficiency (RE) and Adsorption Capacity as a

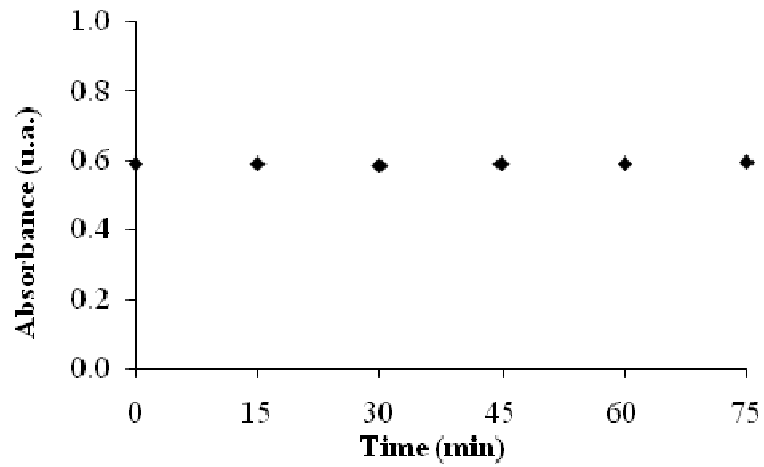
Table 1. Factorial design matrix 3² used in Statistica software

Assays	Input Variables				Output Variables	
	Coded		Actual		Response	
	X ₁ *	X ₂ *	DCA massa (g)	C _o (mg/L)	RE (%)	q _e (mg/g)
1	-1	1	0,2	1000	85,67	128,50
2	-1	-1	0,2	3000	94,89	427,00
3	-1	1	0,2	5000	97,87	734,00
4	0	0	0,6	1000	99,67	49,93
5	0	0	0,6	3000	99,44	149,17
6	0	0	0,6	5000	99,40	248,50
7	1	-1	1,0	1000	100,00	30,00
8	1	-1	1,0	3000	100,00	90,00
9	1	-1	1,0	5000	99,20	148,80

*X₁ represents the mass of DCA, X₂ is the initial concentration (C_o) of ions Cu²⁺.



Graph 1. Calibration curve of Cu²⁺ solutions and absorbance for a λ_{max} of 775 nm



Graph 2. Stability Cu²⁺ solution and absorbance for one λ_{max} 775 nm

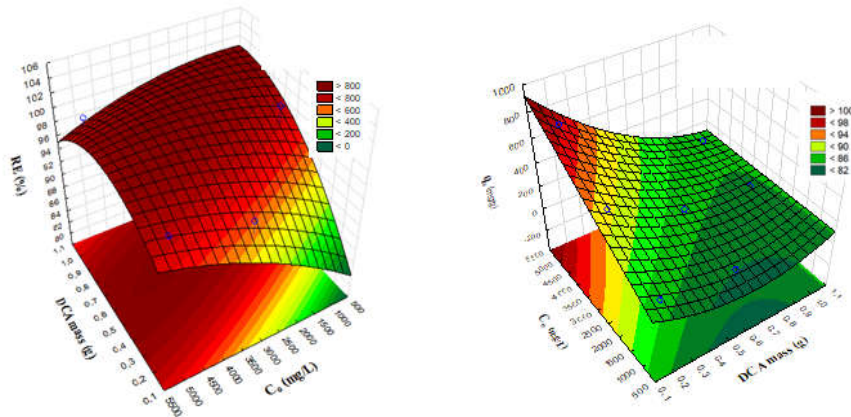


Figure 1. Response surface: a) Removal efficiency (RE) and b) Adsorption capacity (q_e) as a function of DCA mass (g) and initial concentration Cu²⁺

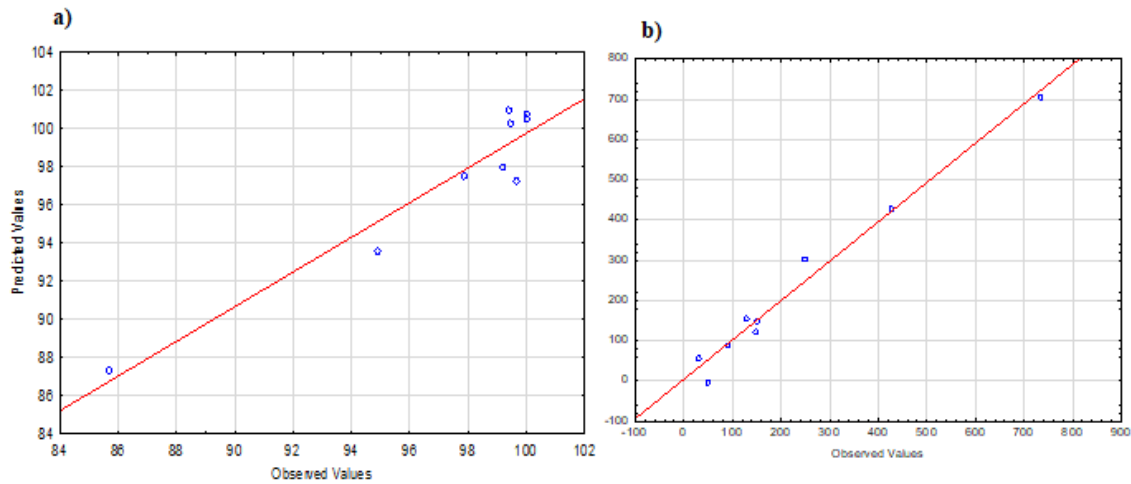


Figure 2. Values predicted by the obtained model versus values observed in the experimental tests, for 95% confidence level: a) Removal efficiency (%) and b) Adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$)

function of DCA mass (m , grams) and initial concentration Cu^{2+} (C_0 , $\text{mg}\cdot\text{L}^{-1}$). In addition to obtaining the response surfaces (Figure 1, a) Removal efficiency and b) Adsorption capacity) that describe the output variables, respectively. It can be seen from Figure 1 a) that the removal efficiency of the copper ions is strongly influenced by the adsorbent mass used in the system, obtaining high efficiency levels (up to 100%) for small quantities (0.1 grams). Similar to Figure 1 b), for adsorbate adsorption capacity, but for initial Cu^{2+} concentration levels greater than $3500 \text{ mg}\cdot\text{L}^{-1}$ and , which corroborates that there are a number of active sites on the surface of the adsorbent for removal of metallic salts present in aqueous medium, which is due to the presence of the functional groups silanol of DCA. The polar groups (hydroxyls) have a well known metal affinity, promoting a better interaction between the metal ion and the adsorbent surface, being the relevant affinity factor for the adsorption process (Ball, 2012). Figure 2 presents the comparison between the values observed in the experimental tests and the predicted values obtained by the models adjusted for 95% confidence level, a) Removal efficiency and b) Adsorption capacity.

Table 2. Chemical composition obtained in the FRX assay for sample the DCA

Compound	Composition mass (%)
SiO_2	61,789
Al_2O_3	10,708
Fe_2O_3	2,894
CaO	7,105
MgO	1,075
SO_3	1,036
K_2O	1,057
BaO	0,764
Na_2O	0,566
Cl	0,477
TiO_2	0,300
P_2O_5	0,057
ZrO	0,045
Sr	0,032
HgO	0,016
MnO	0,017
Co_3O_4	0,014
Cr_2O_3	0,018
ZnO	0,009
NiO	0,004
Br	0,003
Fire loss	12,000
Σ	99,99

From the graphs presented in Figure 2, it is possible to evaluate that both models proposed by equations 3 and 4 (See item 4.3), satisfactorily describe the behavior of the effects caused by the input variables (adsorbent mass and initial concentration of Cu^{2+}) in the output variables (Removal Efficiency and Adsorption Capacity), because the observed points are distributed over the line of the predicted values.

Glossary

PW - Produced Water
 DC - Drilling Cutting
 DCA - Drilling Cutting Ash
 C_0 - Concentration initial of Cu^{2+} ($\text{mg}\cdot\text{L}^{-1}$)
 C_e - Concentration equilibrium of Cu^{2+} ($\text{mg}\cdot\text{L}^{-1}$)
 V - Volume solution (L)
 q_e - Adsorption capacity of ions Cu^{2+} to DCA ($\text{mg}\cdot\text{g}^{-1}$)
 m - mass of DCA (g)
 RE(%) - Removal efficiency (RE) of Cu^{2+}
 RSM - Response Surface Methodology

Conclusion

Based on the results obtained this work, a high adsorptive capacity of the drilling cutting ash is observed in view of the bivalent copper ion removal efficiency high (85.67 to 100%) under mild conditions of temperature, pressure, pH and initial concentration. It also shows a rapid synergy of metal ions adsorption to silanoic groups present on the surface of the DCA. In general, the use of this adsorbent appears as a promising potential in compared to of technologies that use the adsorption process as effluent treatment.

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