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Scientific Paper

Evaluation of the adsorption potential of iron mining tailing and its effect on *raphanus sativus* germination

Avaliação do potencial de adsorção de rejeitos de mineração de ferro e seu efeito na germinação de raphanus sativus

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ABSTRACT

The objective of this work was to evaluate the physicochemical and adsorptive characterization of Fe tailing collected in the district of Brumadinho; and verify its effect on *Raphanus sativus* germination. The material was collected on the surface layer (0-20 cm) and disintegrated for pH, redox potential – Eh, electrical conductivity – EC, OM, cation exchange capacity – CEC, specific surface area – SSA and functional groups characterization. Adsorption studies were conducted using methylene blue (MB). The results of the adsorption studies were analyzed using kinetic models (Elovich, pseudo-first order – PFO and pseudo-second order – PSO) and isotherm models (Freundlich, Langmuir and Sips). The tailing has an acidic pH (5.60), negative ΔpH (-0.30) and low CEC (1.85 $cmol_c\ g^{-1}$). A high MB adsorption efficiency (96%) was verified. The Elovich model ($0.9248<R^2<0.9858$) best represented the chemical kinetics, and the Freundlich model best describes the MB adsorption process in the tailing ($R^2 = 0.9609$). The maximum adsorption capacity (q_m) was equal to 15.08 mg g^{-1}. The presence of Fe tailing positively influenced the germination of *R. sativus* seeds (73.8%), but stem and root growth were inferior when compared to seedlings cultivated in compost substrate. It is concluded that the material has favorable cationic adsorption capacity, which can benefit soil fertilization. However, *R. sativus* development was minor in Fe tailing substrate, probably due to low CEC, OM and nutrient availability.

Keywords: chemical kinetics; adsorption isotherms; methylene blue; B1 dam; plant development; radish.

RESUMO

O objetivo deste trabalho foi avaliar a caracterização físico-química e adsortiva do rejeito de Fe coletado no distrito de Brumadinho; e verificar seu efeito na germinação de *Raphanus sativus*. O material foi coletado na camada superficial (0–20 cm) e desintegrado para determinação de pH, potencial redox (Eh), condutividade elétrica (EC), matéria orgânica (MO), capacidade de troca catiônica (CEC), área superficial específica (SSA) e de grupos funcionais. Estudos de adsorção foram conduzidos utilizando azul de metileno (MB). Os resultados dos estudos de adsorção foram analisados utilizando modelos cinéticos (Elovich, pseudoprimeira ordem – PFO e pseudossegunda ordem – PSO) e modelos isotérmicos (Freundlich, Langmuir e Sips). O rejeito apresenta pH ácido (5,60), ΔpH negativo (-0,30) e baixa CEC (1,85 cmolc g^{-1}). Foi verificada alta eficiência de adsorção de MB (96%). O modelo de Elovich ($0,9248 < R^2 < 0,9858$) representou melhor a cinética química e o modelo de Freundlich descreveu melhor o processo de adsorção de MB no rejeito ($R^2 = 0,9609$). A capacidade máxima de adsorção (q_m) foi igual a 15,08 mg g^{-1}. A presença de rejeito de Fe influenciou positivamente a germinação de sementes de *R. sativus* (73,8%), mas o crescimento do caule e da raiz foi inferior quando comparado às mudas cultivadas em substrato composto. Conclui-se que o material tem capacidade de adsorção catiônica favorável, o que pode beneficiar a fertilização do solo. No entanto, o desenvolvimento de *R. sativus* foi menor no substrato de rejeito de Fe, provavelmente devido à baixa CTC, MO e disponibilidade de nutrientes.

Palavras-chave: cinética química; isotermas de adsorção; azul de metileno; barragem B1; desenvolvimento vegetal; rabanete.

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INTRODUCTION

Mining is the main economic activity in the state of Minas Gerais (Brazil), corresponding to more than 40% of the revenue of the national mining industry (IBRAM, 2023). Iron (Fe) mining alone corresponds to 45% of the value of mineral production sold in Brazil (RMMG, 2015). Mining provides raw materials for different industries in the global economy (Mendes *et al.*, 2022). However, during mining activities, large quantities of soil and rocks are used to extract metallic Fe ore, generating waste. Additionally, during the ore processing, mining tailing is generated. The tailing produced in the processes is commonly stored in dams and is predominantly composed of Fe ore, quartz, and water.

Tailing dams are reservoirs designed to retain solid tailings and water from mining processes. Although these structures are designed to outlast their useful life, tailing dams are subject to failure. The causes of failure are numerous, and include foundation failure, slope instability, dam overtopping or overflowing, mine subsidence, meteorological causes (such as heavy rains, hurricanes, rapid melting, ice accumulation in the tailing dam), infiltration or piping, seismic liquefaction, construction deficiency (structural failure) and operation management (Mendes *et al.*, 2022).

Tragedies involving tailing dams cause considerable social, economic, and environmental impacts. In the state of Minas Gerais, two dam failures occurred in a period of three years, both with devastating environmental consequences (Mendes *et al.*, 2022). The last event was in 2019, when the Córrego do Feijão B1 dam in the city of Brumadinho released more than 12 million m^3 of mining tailings into the Ferro Carvão River (Kobayashi *et al.*, 2023; Thompson *et al.*, 2023).

The dam failure released a rapid and turbulent tailing flow that destroyed downstream infrastructure and spread tailings throughout the Ferro Carvão and Paraopeba river basin, affecting an area of approximately 300 hectares (Kobayashi *et al.*, 2023). After drying, the material became rigid and compact, altering the composition, structure, and fertility of the local soil, due to the high concentration of Fe oxides and fine grains (Almeida *et al.*, 2018; Pacheco *et al.*, 2023). Additionally, potentially toxic metals (MPT), such as cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), and manganese (Mn), were incorporated into the affected environment, altering the environmental quality (Pacheco *et al.*, 2023; Silva *et al.*, 2023).

Several studies were conducted to understand the implications of tailings in biodiversity and physicochemical parameters of the affected water bodies and soils (Mendes *et al.*, 2022; Siqueira *et al.*, 2022; Kobayashi *et al.*, 2023; Mendes *et al.*, 2023; Pacheco *et al.*, 2023; Thompson *et al.*, 2023). The soil, one of the most affected environmental compartments, had its chemical composition (incorporation of Fe minerals, change in cation exchange capacity – CEC and pH) and structure (density, particle size change and reduction in porosity) altered (Embrapa, 2017; Almeida *et al.*, 2018; Pacheco *et al.*, 2023). The mixing of Fe ore tailings with uncontaminated grabbed soil changed soil composition, enriching the contents of Fe, Mn, aluminum - Al and phosphorus - P, and slightly decreasing density (Pacheco *et al.*, 2023). These changes affected land use possibilities, resulting in changes in nutrient-plant interactions and agricultural difficulties (Almeida *et al.*, 2018).

Soils play an essential role in all ecological cycles of nature and provide physical support and nutrients to plants (Silva *et al.*, 2023). Environmental changes and stress factors can severely impact plant growth and development. Nutrient is available in soils mainly through the adsorption process, which is affected by environmental changes, such as pH, CEC, redox potential (Eh), electrical conductivity (EC) and organic matter (OM). Fe ore tailings present in the surficial portion of the soil of Paraobepa and Ferro Carvão basin have altered these conditions. The physical properties and chemical composition of tailings from mining activities depend on ore composition, extraction process, and weathering during tailings storage (Cruz *et al.*, 2020). Soils contaminated with Fe ore tailings generally have low OM content, low CEC, large amounts of fine particles and high concentrations of some metals (Cruz *et al.*, 2020). A previous characterization of the tailings from Brumadinho showed that the residue is basically composed of Al, Fe and Mn oxides, and silt grained (Pacheco *et al.*, 2023; Silva *et al.*, 2023).

Thus, the incorporation of Fe ore tailings can negatively affect the soil cation retention capacity, implicating a loss in nutrient availability to plant. In this context, it is necessary to comprehend the adsorption capacity of the affected ecosystems. This property facilitates the understanding of possible transfer mechanisms of essential elements in the soil (Almeida *et al.*, 2018). Adsorption mechanisms are often analyzed using isotherm models such as Freundlich, Langmuir, and Temkin (Majd *et al.*, 2022; Xue *et al.*, 2022; Hu *et al.*, 2023). The adsorption isotherm describes and predicts the amount of material adsorbed as a function of pressure (or concentration) at a constant temperature (Majd *et al.*, 2022). Furthermore, kinetic models can be applied to understand adsorption reaction rates.

Additionally, the changes in the soil compartment after the B1 dam rupture negatively affected soil biota. Silva *et al.* (2023) showed that earthworms lost weight when the percentage of mining waste increased, and that *E. foetida* presented DNA damage in the contaminated soils of Brumadinho. Low reproduction levels of *C. vulgaris* tested in materials (soil and Fe ore tailings) collected after the B1 rupture were determined by Siqueira *et al.* (2022). However, the implications of Brumadinho Fe ore tailings on plant growth were not found in the literature review.

The cultivation of economic crops in the mine tailings can produce biomass of industrial interest and contribute to the socio-economic development of these mining areas (Liu *et al.*, 2022). The plant species *Raphanus sativus* (radish) is of great economical and nutritional importance, and well-known for its bioaccumulation capabilities, being a potential biosafety indicator for growing crop species in soils contaminated with mining tailings (Araújo *et al.*, 2022). To better comprehend the adsorption characteristics of the Fe tailing disposed in Brumadinho and its implication in *R. sativus* germination and growth, the objective of this work was to evaluate the adsorption capacity of the Fe tailing collected after the failure of the B1 dam on cationic dye (methylene blue – MB), a commonly used regent to determining CEC in soils.

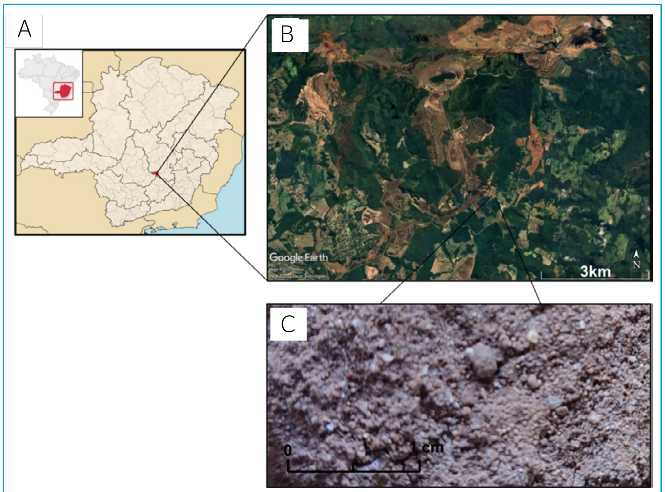
METHOD

Sample collection and preparation

The samples were collected in August 2019, in the surface layer (0-20 cm), in Brumadinho (MG) and stored in polyethylene bags. For the experimental procedures, the samples were air-dried, crushed with a ceramic mortar, and homogenized using the elongated pile method (Petersen, 2004). The study samples were collected in the municipality of Brumadinho, in Minas Gerais, at coordinates 20°08 ‘06” S, 44°06’ 48” W (Figure 1).

Characterization of iron mining tailing

The methods used to characterize the tailing were pH, redox potential (Eh), electrical conductivity (EC), organic matter (OM), cation exchange capacity (CEC), specific surface area (SSA), and functional groups. The procedures are presented in Table 1. All assays were performed in triplicates.



Source: authors (2023).

Figure 1 – Location map of the study area: (A) municipality of Brumadinho; (B) sample collection point and (C) sample collected.

Chemical kinetics studies

Batch tests were performed to determine the influence of time and dye concentration during sorption studies (Roy *et al*., 1991). The tests were carried out at room temperature (26°C), using 250 mL Erlenmeyer flasks, Fe mining tailing (0.50 g, 1.00 g, 2.00 g and 4.00 g) and MB solution (100 mL, 130 mg L^{-1}). These concentrations were selected based on the results obtained by Almeida *et al*. (2018) using Fe mining waste collected in the municipality of Mariana (MG).

The system was shaken on an orbital shaker at a frequency of 100 rpm. Samples were taken at times 1, 5, 15, 30, 60, 120, and 240 minutes to verify the influence of contact time on adsorption. MB absorbance was determined using UV-VIS (model K37-UVVIS from KASVI, with photometric precision of 0.5%) and a quartz cuvette with an optical path length of 10.0 mm. The concentration was obtained using Lambert-Beer Law (Equation 1). The analytical curve and absorbance spectra are available in Figures 2A and 2B, respectively.

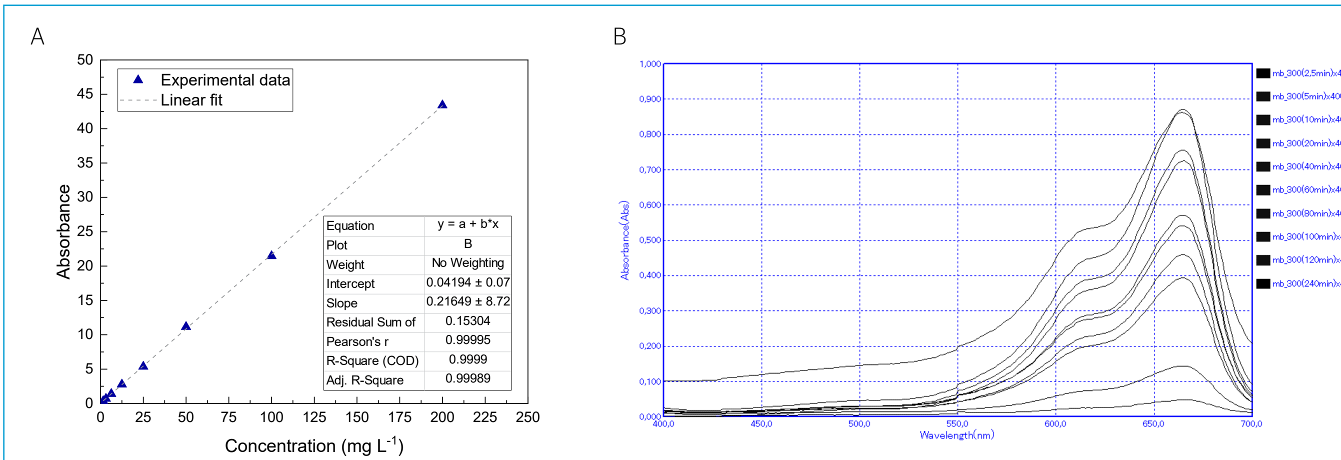
$$A = \varepsilon b C \quad (1)$$

Where A is the absorbance, ε is the MB molar absorptivity, b is the optical path length of the quartz cuvette, and C is the concentration.

The removal efficiency (R%) and adsorption capacity at time t, q_t (mg g^{-1}) were calculated using Equations (2) and (3), respectively:

Table 1 – Physicochemical characterization analysis.

Assay	Description	Reference
pH, Eh	Distilled water and tailing solution (1:2.5) were kept under constant stirring for 5 min and rested for 60 min until pH (precision ± 0.01) and Eh (precision ± 2 mV) determination using pHmeter from Bel Engineering	Embrapa (2017)
EC	Distilled water and tailing solution (1:1) were kept under constant stirring for 5 min and rested for 60 min until EC (precision ± 1%) determination with a conductivity meter from Bel Engineering	Camargo *et al.* (2009)
OM	Hydrogem peroxide reaction	Eusterhues, Rumpel, and Kögel-Knabner (2005)
CEC, SS	Methylene blue adsorption test	Arab, Araújo, and Pejon (2015)
Functional groups	Fourier Transform Infrared Spectrometer (FTIR) was performed with a Shimadzu IRP Pretige-41 spectrophotometer. The sample was mixed with potassium bromide (KBr) to form pellets and subsequently subjected to analysis. The spectrum was performed in the range from 400 to 4000 cm^{-1}	Silverstein *et al.* (2014)



Source: authors (2023).

Figure 2 – Methylene blue (A) analytical curve (absorbance vs. concentration) and (B) absorbance spectra.

$$R\% = \frac{100x(C_0 - C_t)}{C_0} \quad (2)$$

$$q_t = \frac{Vx(C_0 - C_t)}{m} \quad (3)$$

Where C_0 and C_t are the initial MB concentration (mg L^{-1}) and MB concentration at time t (mg L^{-1}), respectively. V is the volume of the MB solution (L), and m is the Fe tailing mass (g).

Data from the kinetic experiments were analyzed using three nonlinear kinetic models (pseudo-first order - PFO, pseudo-second order - PSO, and Elovich). Origin 9.1 software was used to model the experimental data. These models were selected because they are widely used to understand the sorption mechanisms of a wide range of adsorbents and contaminants (Almeida *et al.*, 2018; Lima *et al.*, 2022; Raimondi *et al.*, 2022; Kasemodel; Romão; Papa, 2024).

The PFO, PSO, and Elovich models are presented in Equations 4, 5 and6, respectively:

$$q_t = q_{e(1-\exp(-k_{p1}t))} \quad (4)$$

$$q_t = \frac{q_e^2 k_{p2} t}{1 + q_e k_{p2} t} \quad (5)$$

$$q_t = \frac{1}{b} \ln(1 + abt) \quad (6)$$

Where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the adsorption capacity at time (t) and at equilibrium, respectively; kp_1 (L min^{-1}) and kp_2 (g mg^{-1} min^{-1}) are the PFO and PSO rate constants, respectively; t is time (min); a is the initial velocity due to dq/dt with $q_t = 0$ (mg g^{-1} min^{-1}); and b is the desorption constant of the Elovich model (g^{-1} mg^{-1}).

Equilibrium studies

Equilibrium experiments were conducted at room temperature (26°C) for 24 h. The Fe mining tailing mass was varied (0.50 g, 1.00 g, 2.00 g and 4.00 g), MB concentration was maintained at 130 mg L^{-1}, and the solution volume was 100 mL. The removal efficiency, R_e, and the adsorption capacity at equilibrium conditions, q_e (mg g^{-1}), were calculated using Equations 7 and 8, respectively:

$$R_e\% = \frac{100x(C_0 - C_e)}{C_0} \quad (7)$$

$$q_e = \frac{Vx(C_0 - C_e)}{m} \quad (8)$$

Where C_0 and C_e are the initial concentration of MB (mg L^{-1}) and the equilibrium concentration of MB (mg L^{-1}), respectively. V is the volume of the solution containing MB (L), and m is the Fe tailing mass (g).

Equilibrium experimental data were modeled using the Langmuir, Freundlich, and Temkin models, which were implemented to fit the dye adsorption isotherm data. The different types of isotherms occur mainly due to the difference in adsorption mechanisms, which can be used to identify the nature of adsorption (Hu *et al.*, 2023).

The parameters of each model were obtained using the nonlinear form of the equation for each model with Origin 9.1 software. The Levenberg Marquardt integration algorithm and simplex interaction were used. The nonlinear forms of Langmuir, Freundlich, and Temkin are presented in Equations 9, 10 and 11, respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (9)$$

$$q_e = K_F \; C_e^{1/n} \quad (10)$$

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (11)$$

Where C_e (mg L^{-1}) is the equilibrium concentration; q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium; q_m (mg g^{-1}) and K_L (L mg^{-1}) are Langmuir constants related to adsorption capacity and adsorption energy, respectively; K_F (mg L^{-1})(L mg^{-1}) is the Freundlich adsorption constant; 1/n is a measure of adsorption intensity; b (J mol) is the Temkin constant related to the heat of adsorption; K_T (L mg^{-1}) is the Temkin constant; R is the universal ideal gas constant (8.31 J mol^{-1} K^{-1}); T (K) is the absolute adsorption temperature.

Statistical analysis

The experimental data fitted to the models were analyzed using the coefficient of variation (R^2) (Equation 12) to evaluate the validity and performance of the isotherm and kinetic models. A higher R^2 value indicates a better correlation between experimental data and theoretical models.

$$R^2 = \frac{\sum(q_{mean} - q_{cal})^2}{\sum(q_{cal} - q_{mean})^2 + \sum(q_{cal} - q_{exp})^2} \quad (12)$$

Raphanus sativus germination and growth test

The seed germination and root elongation assay were conducted with Indra radish microgreen seeds (*R. sativus* from Isla Sementes). Fe tailing from Brumadinho and compost (Mogifertil brand) were used as substrates. The substrates were placed in Petri dishes, moistened with distilled water, and kept at room temperature (26°C). 20 seeds were planted (spaced approximately 1 cm apart) on each plate, totaling 80 seeds in tailing substrate and 80 seeds in compost substrate. Substrates were moistened daily.

Germination counts were conducted daily until the end of the experiment (10 days). After 10 days, root and stem length were measured, and the wet mass of the seedlings was determined.

RESULTS AND DISCUSSION

Physicochemical characterization

The results of the physicochemical characterization of Fe tailing collected from Brumadinho are available in Table 2.

Fe tailing presented acidic pH (H_2O). These data are in accordance with those obtained by Siqueira *et al.* (2022), whose study reports an average of 4.6 ± 0.5 (n = 16) for the pH of tailing samples collected in Brumadinho, with values varying between 4.1 and 5.8. The ΔpH values indicate the charge balance on the grain surfaces. The ΔpH value was -0.3, which indicates that the charge net on the surface is negative, that is, the material is predisposed to retaining cations.

Measurements of redox potential (Eh), in addition to pH, are widely used for environmental monitoring since several reactions that occur in the soil take place through the transfer of electrons. Eh value is +91.50 mV ± 0.71, which indicates that the Fe tailing is an oxidizing environment, favoring the presence of Fe oxides. High concentrations of Fe oxides can intensify the adsorption of metals (Embrapa, 2021).

CEC (1.85 $cmol_c$ kg^{-1} ± 0.04) are classified as low, according to the classification proposed by Catani and Jacinto (1974). The result is consistent since tailing is mainly constituted of quartz with a concentration of OM. The SSA is an indication of the surface area of the material. When the SSA is greater, the presence of adsorption sites is expected.

The average EC of the material is 374 µS cm^{-1}. The EC indicates the presence of ions in the solution and can serve as an indication of changes, such as the presence of contaminants.

Figure 3 shows the FT-IR spectrum. The bands 1200–1000 cm^{-1} correspond to Si-O-Si, and the bands 550–400 cm^{-1} correspond to Fe-O (Coura *et al.*, 2021). These bands were also detected by Coura *et al.* (2021) in a study with Fe mining tailing. The presence of these bands may be associated with quartz, goethite, and hematite found in Fe mining waste (Almeida *et al.*, 2018).

Table 2 – Physicochemical characterization of Fe tailing from Brumadinho.

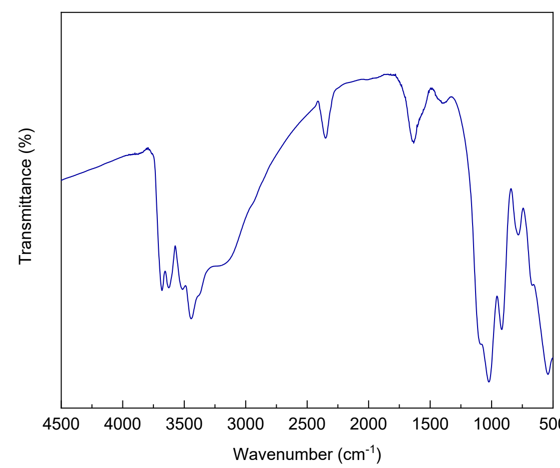
Parameters	Value (n = 3)
pH_{H2O}	5.60 ± 0.00
pH_{KCl}	5.30 ± 0.00
ΔpH	-0.3 ± 0.00
Eh [mV]	+91.50 ± 0.71
EC [µS cm^{-1}]	374.50 ± 45.96
OM [mg g^{-1}]	0.02 ± 0.00
CEC [$cmol_c$ kg^{-1}]	1.85 ± 0.04
SS [m^2 g^{-1}]	14.45 ± 0.28

Influence of time and adsorbent mass on the adsorption process

The influence of adsorbent mass and time on the adsorption process is available in Figure 4.

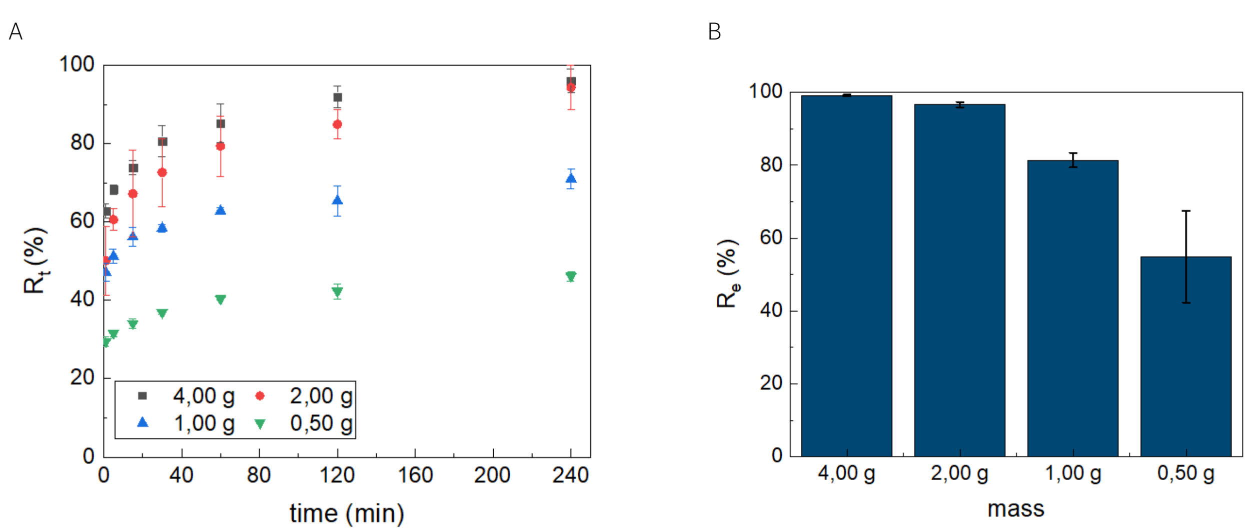
Figure 4A illustrates the influence of time on the percentage of MB adsorbed. Equilibrium was reached in approximately 120 minutes. A change in the MB adsorption rate is noted between tailing dosages of 5 and 10 g L^{-1} and 20 and 40 g L^{-1}. When lower dosages were used (5 and 10 g L^{-1}), the saturation rate obtained was less than 65% in the first 120 minutes of testing, while when using higher dosages (20 and 40 g L^{-1}) the saturation rate exceeded 80% in the first 120 minutes of testing. According to Almeida *et al.* (2018), the equilibrium time was reached in 200 minutes when evaluating the MB adsorption process in Fe mining tailings from the Fundão dam, in Mariana (Minas Gerais).

The contact time between the adsorbent and the adsorbate is important to indicate the time until reaching the equilibrium condition. In this study,



Source: authors (2023).

Figure 3 – FT-IR spectrum of Fe mining tailings.



Source: authors (2023).

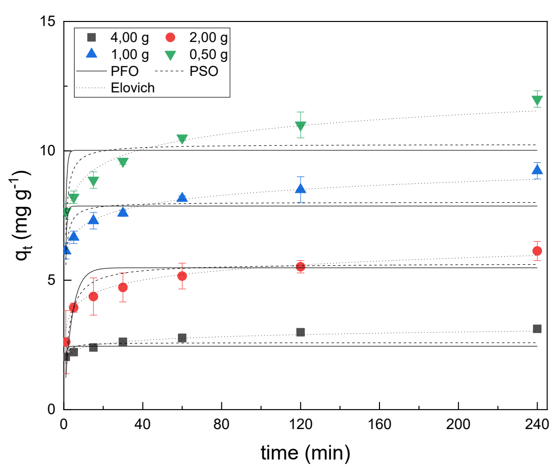
Figure 4 – Influence of (A) time and (B) adsorbent mass on the MB adsorption process in Fe mining tailings.

to ensure that this condition was achieved, it was decided to conduct the tests for 24 hours.

Figure 4B illustrates the effect of the adsorbent mass on the percentage of MB adsorbed in the equilibrium condition. The percentage of MB removed increases with the rising adsorbent dosage. This higher efficiency may be due to a greater availability of adsorption sites when using a larger adsorbent dosage (especially 20 and 40 g L^{-1}). Almeida *et al.* (2018) found that when the adsorbent dosage was greater than 200 g L^{-1}, the MB adsorption efficiency was close to 90%. In this study, adsorption efficiency was 96% when the adsorbent dosage used was 40 g L^{-1}.

Chemical kinetics studies

The chemical kinetic data curves were conducted using different adsorbent masses (4.00 g, 2.00 g, 1.00 g, and 0.50 g). The data fitted to the PFO, PSO, and Elovich models are shown in Figure 5, and the parameters obtained are described in Table 3.



Source: authors (2023).

Figure 5 – PFO, PSO, and Elovich kinetic models applied to experimental data.

When less mass of mining tailing was used, the adsorption capacity (q_e) was greater. Furthermore, it was found that the q_e values obtained from PFO and PSO models were similar, like the data obtained by Almeida *et al.* (2018).

Based on R^2 and R_{ajd}^2, the Elovich model presented a better fit to the experimental data, indicating that the activation energy increases as the sorption time grows, and that the adsorbent surface is heterogeneous.

As higher values of R^2 indicate a better correlation between experimental data and theoretical models, the adequacy of the evaluated kinetic models follows the subsequent trend for all Fe tailing tested masses (4.00 g, 2.00 g, 1.00 g, and 0.50 g): Elovich > PSO > PFO.

According to Almeida *et al.* (2018), the PSO and PFO models showed a good fit to MB adsorption onto Fe mining tailings data. However, the authors did not evaluate the Elovich model. The authors also found that q_e increased when the initial MB concentration was higher. Almeida *et al.* (2018) obtained q_e values of 5.15 mg g^{-1} (PFO) and 5.34 mg g^{-1} (PSO) when the initial MB concentration was 200 mg L^{-1} and Fe mining tailing dosage was 40 g L^{-1}. In the present study, it was found that when the adsorbent dosage was reduced, the q_e values were higher. Values of 10.02 mg g^{-1} (PFO) and 10.26 mg g^{-1} (PSO) were obtained when the initial concentration of MB was 130 mg L^{-1}, and the adsorbent dosage was 5 g L^{-1}.

MB adsorption isotherms

To understand the association between the amount of MB adsorbed per mass of Fe mining tailings and the concentration of MB in solution at equilibrium, three different types of adsorption isotherms were applied and verified. Results of the data applied to the Langmuir, Freundlich, and Temkin models are available in Figure 6 and the isotherm parameters are presented in Table 4.

The Freundlich model (R^2 = 0.9609) presented the best fit to the experimental data, followed by the Temkin (R^2 = 0.9072) and Langmuir (R^2 = 0.8784) models, respectively.

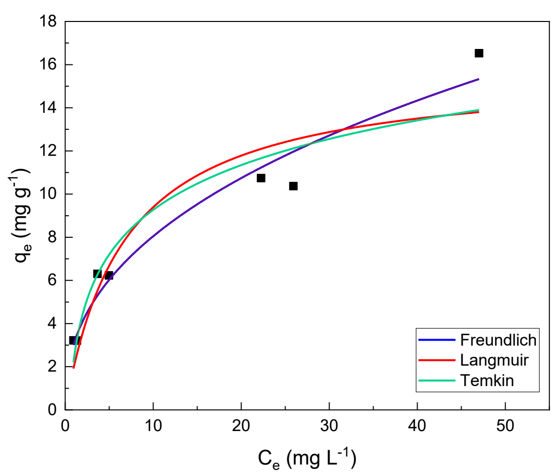
The Freundlich isotherm is a widely used empirical equation, applicable in adsorption studies on heterogeneous surfaces. This isotherm model has

Table 3 – Comparison of kinetic models applied to MB adsorption onto Fe tailings.

Model	Parameters	Mass			
		0.50g	1.00g	2.00g	4.00g
PFO	q_e (mg g^{-1})	10.02 ± 0.37	7.87 ± 0. 24	5.48 ± 0.23	2.45 ± 0.14
	k_{p1} (min^{-1})	1.42 ± 0.71	1.50 ± 0.63	0.25 ± 0.04	1.78 ± 0.77
	R^2	0.2747	0.3264	0.8240	0.2398
	R_{adj}^2	0.1297	0.1917	0.7889	0.0878
PSO	q_e (mg g^{-1})	10.26 ± 0.34	8.02 ± 0.22	5.66 ± 0.18	2.59 ± 0.15
	k_{p2} (g mg^{-1} min^{-1})	0.19 ± 0.11	0.29 ± 0.15	0.08 ± 0.02	1.05 ± 0.64
	R^2	0.5078	0.5552	0.9083	0.4662
	R_{adj}^2	0.4093	0.4663	0.8900	0.3594
Elovich	a (mg g^{-1} min^{-1})	**3919.23**	**16449.41**	**167.28**	**3221.46**
	b (g mg^{-1})	**5.00 ± 0.50**	**1.89 ± 0.09**	**1.77 ± 0.16**	**4.99 ± 0.50**
	R^2	**0.9374**	**0.9599**	**0.9882**	**0.9527**
	R^2_{ajd}	**0.9248**	**0.9519**	**0.9858**	**0.9432**

Note: The data in bold represent the models with the best fit to the experimental data.

two parameters, K_F and n. The first parameter represents the adsorption force, while the second corresponds to the heterogeneity of the adsorbent surface (Majd *et al.*, 2022). These values are subject to variations according to conditions of temperature, pH, and adsorbent mass, among others (Chen *et al.*, 2021). The Freundlich model can describe the heterogeneity of the surface, through the parameter n (Freundlich isotherm adjustment constant). On homogeneous surfaces, n is equal to 1 and the model presents a linear curve (Majd *et al.*, 2022). This parameter shows the proportionality between adsorption and the percentage of occupied sites. When n is greater than 1, adsorption is favorable; and when $0 < n < 1$, adsorption is not favorable (Gheibi *et al.*, 2022). In this study, the obtained value of n was 0.42.



Source: authors (2023).

Figure 6 – Freundlich, Langmuir, and Temkin isotherm models applied to experimental data.

Table 4 – Comparison of isotherm models obtained from MB adsorption onto Fe tailings.

Model	Parameter	Value
Langmuir	q_m (mg g^{-1})	15.08 ± 2.15
	K_L (L g^{-1})	0.15 ± 0.07
	R²	0.8784
Freundlich	K_F (mg g^{-1})	**3.08 ± 0.47**
	n	**0.42 ± 0.05**
	R²	**0.9609**
Temkin	b (J mol^{-1})	2.78 ± 0.40
	K_T (L g^{-1})	2.22 ± 0.97
	R²	0.9072

Note: The data in bold represents the model with the best fit to the experimental data.

The Temkin model is interpreted by the reduction in enthalpy in the adsorption process (Gheibi *et al.*, 2022). The b parameter is associated with adsorption heat, and when this value is less than 8 kJ mol^{-1}, surface adsorption occurs physically (Gheibi *et al.*, 2022). In this study, b value was 2.78 kJ mol^{-1}, indicating that adsorption occurs physically.

Finally, the Langmuir model assumes monolayer adsorption and is widely used to predict q_m. From the experimental data, the maximum adsorption capacity (monolayer) was equal to 15.08 mg g^{-1}. This model assumes that adsorption and desorption rates at equilibrium are equal; and K_L refers to the ratio between adsorption and desorption rates, which is a measure of the strength at which MB molecules are adsorbed on the surface of Fe mining tailings.

Table 5 presents the q_m values obtained in MB adsorption studies on mining waste. In the present study, the potential for MB adsorption on raw Fe mining tailing was evaluated. It is noted that the adsorption potential is higher than that found by Almeida *et al.* (2018) in Fe mining tailing collected in the municipality of Mariana (MG). A higher q_m implicates a greater capacity for retention of cationic molecules by Fe tailing, which can favor soil nutrition. Physicochemical characteristics of this material, such as low CEC and OM content, may have contributed to a lower adsorption capacity. However, the use of cationic fertilizations in dosages like q_m may benefit sediment nutrition and plant growth and minimize losses by leachate.

Raphanus sativus germination and growth assay

The results obtained from the germination assay area are presented in Table 6 and Figure 7. The effect of Fe tailings affected positively the germination of *R. sativus*, with an equivalent of 73.8% tax of germination. However, it is possible that the limited nutrient availability restricted the development of the seedlings. The measurements of stem and root in seedlings developed in Fe tailing substrate were significantly lower than in seedlings developed in compost. The smaller tax of seed germination developed in compost can be attributed to limitations in space, but further studies must be carried out.

Radish plants cultivated in Fe ore tailings presented lower biomass production, stem, and root length. These results are like those obtained by Araújo *et al.* (2022) using *R. sativus* seeds in Fe ore tailings collected from the Fundão dam rupture, in Mariana (state of Minas Gerais). According to the authors, individual radish plants cultivated in the substrate without mining tailings developed better. Additionally, radishes cultivated in soil substrate developed more leaves, presented larger total leaf area and higher biomass production.

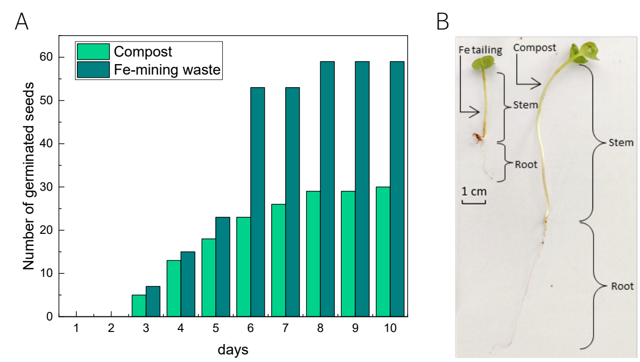
According to Cruz *et al.* (2020), the Fe ore tailings released by the rupture of the Fundão dam interfered with the growth of native Atlantic Forest plant species. Reduced plant growth was due to nutritional limitation, caused by low nutrient availability, low OM content and low CEC of the tailings (Cruz *et al.*, 2020). The use of plant growth regulators may be an alternative to increase biomass production. According to Santana *et al.* (2020), the

Table 5 – Comparison of the maximum adsorption capacity value obtained by the Langmuir model in MB adsorption studies using mining waste.

Adsorbent	q_m (mg g^{-1})	Reference
Fe mining tailing	15.08	This study
Tin Mining Tailings Geopolymer	30.31	Fatimah *et al.* (2023)
Nanoscale zero-valent iron produced from Fe mining waste	163.93	Han *et al.* (2023)
Fe mining tailing	4.42	Almeida *et al.* (2018)

Table 6 – Germination parameters of Raphanus sativus.

Parameter	Compost	Fe tailing
Number of seed germinations in 10 days	30	59
Percentage of seed germination in 10 days (%)	37.5	73.8
Stem medium length (cm)	4.64 ± 1.89	2.18 ± 0.55
Root medium length (cm)	4.25 ± 2.54	1.03 ± 0.75
Mass (g)	4.15	3.21



Source: authors (2023).

Figure 7 – (A) Germination rate data and (B) differences in Raphanus sativus growth after 10 days.

use of plant growth regulators in Fe ore tailings from the municipality of Mariana (MG) increased biomass production and the accumulation of nutrients. For the Brumadinho tailings, it is recommended that, if cationic plant regulators are applied to the affected area, the dosage use does not surpass the adsorption capacity of the material. Higher dosages may implicate economic losses and contamination.

CONCLUSIONS

In this study, Fe mining tailing collected from Brumadinho (MG) was characterized and its adsorption potential was evaluated. It is concluded that the sample is acidic, has a negative ΔpH, oxidizing Eh, low CEC and low OM content.

The Elovich model presented the best fit to the experimental data. Thus, the activation energy tends to rise as sorption time increases. Additionally, the adsorbent surface can be considered heterogeneous. In equilibrium tests, the Freundlich model presented the best fit, and the q_m obtained was equal to 15.08 mg g^{-1}.

Fe tailings released by the rupture of the B1 dam interfered with the growth of *R. sativus*. Reduced plant growth can be due to nutritional limitations, caused by low nutrient availability, low CEC and low OM content of the tailings.

AUTHOR'S CONTRIBUTIONS

Martins, R.S.A.: Investigation, Methodology, Writing – original draft. Silva, M.R.M.: Investigation, Methodology, Writing – original draft. Lourenço, M.A.S.: Investigation, Methodology, Writing – original draft. Kasemodel, M.C.: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – review & editing.

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