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Removal of eriochrome black T from aqueous solution using coffee husk as bioadsorbent

[1]Nathan Almeida Amancio, [2]Poliana Coste e Colpa, [3]Cíntia Moda Salatino Guardabaxo, [4]Carla Beatriz Silva, [5]Leandro Gustavo da Silva

[1] Instituto Federal de Educação, Ciências e Tecnologia do Sul de Minas Gerais – Campus Muzambinho, amancionat@gmail.com
[2] Instituto Federal de Educação, Ciências e Tecnologia do Sul de Minas Gerais – Campus Muzambinho, poliana.colpa@muz.ifsuldeminas.edu.br
[3] Instituto Federal de Educação, Ciências e Tecnologia do Sul de Minas Gerais – Campus Muzambinho, cintiamoda@gmail.com
[4] Instituto Federal de Educação, Ciências e Tecnologia do Sul de Minas Gerais – Campus Muzambinho, carla.silva@sou.unifal-mg.edu.br
[5] Instituto Federal de Educação, Ciências e Tecnologia do Sul de Minas Gerais – Campus Muzambinho, leandro.silva@muz.ifsuldeminas.edu.br

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Abstract

The eriochrome black T dye belongs to the azo dye class and is often used as an indicator in complexometric titrations and as a fiber dye in industrial processes. It constitutes a direct threat to human health and the environment due to its toxic and carcinogenic nature. Separating this dye from wastewater is essential before its release into water bodies. In this work, the adsorption capacity of eriochrome black T in aqueous solution conferred on the chemically modified or unmodified coffee husk fibers was evaluated. Adsorption experiments were performed in triplicate and batch. The results obtained were adjusted and presented as adsorption isotherms using the Langmuir-Freundlich model. The mass value of adsorbed dye was 483.9 mg ± 17.35 mg and 547.2 mg ± 22.98 mg of eriochrome black T per gram of unmodified and chemically modified coffee husk, respectively, indicating great potential of coffee husk as an adsorbent for the removal of anionic azo dyes in aqueous solution.

Keywords: Bioadsorption. Dye. Isotherm. Contamination.

Introduction

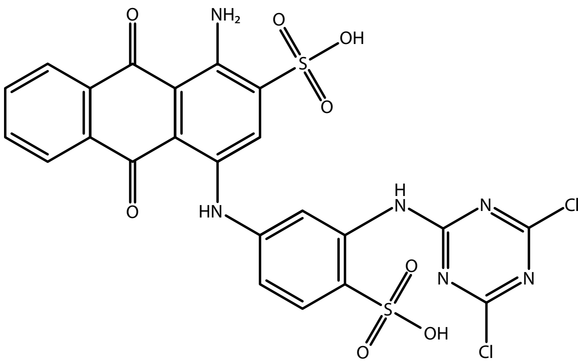
Reactive dyes, characterized by containing a reactive electrophilic group, are widely used in Brazil for cotton dyeing. This type of dye, which includes chromophore groups such as azo and anthraquinone, performs direct chemical reactions by replacing the nucleophilic group with the hydroxyl group of cellulose. These dyes play a preponderant role in the Brazilian cotton dye scenario (ROYER, 2012). According to recent research, approximately 12 % of textile dyes are lost during manufacturing and processing processes, while about 20 % are discarded as industrial effluents (CALVETE, 2011).

The growing concern about the contamination of aquatic environments by toxic dyes reflects the intrinsic ability of these compounds to cause significant environmental damage (BRANDT; UMBUZEIRO; ALBUQUERQUE, 2021). This phenomenon results in decreased water transparency, hindering the penetration of solar radiation and, consequently, reducing the photosynthetic activity of plants (LALNUNHLIMI; KRISHNASWAMY, 2016). In addition, the presence of these dyes can cause adverse effects on human health, such as allergies, skin irritations, cancer and genetic mutations, particularly when contaminated water is used for human consumption (GUARATINI; ZANONI, 2000; YAGUB; SEN; ANG, 2012).

The black dye of eriochrome T (NET), also known as sodium [1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonate] according to the rules of the International Union of Pure and Applied Chemistry (IUPAC); $C_{20}H_{12}N_3NaO_7S$, 461.68 g^{mol-1} ; $\lambda max =$ 612 - 616 nm; is extremely toxic to living beings (BARKA *et al*., 2011; DELLAMATRICE, 2005), causing long-lasting effects. Its molecular structure can be seen in Figure 1.

Given the potential contamination of waters by dyes, especially when destined for public supply,

Figure 1. Chemical structure of eriochrome black T dye.



Source: Prepared by the authors.

it is imperative to adopt efficient technologies for the removal of these contaminants. Wanga and Chen (2006) indicate that conventional water treatment methods exhibit limited effectiveness in removing textile dyes, in addition to having a high cost, motivating the exploration of diverse techniques (DA SILVA *et al*., 2018; ODY; FÉLIS; HARO, 2014).

Several techniques, alone or in combination, have been employed for the removal of dyes in water, including photocatalytic degradation, oxidation, membranes, ozone, and adsorption. Adsorption stands out as one of the most widely used methods due to its efficiency, capacity and large-scale applicability (SALMAN; AL SAAD, 2012).

Biosorption is characterized by the use of natural residues as adsorbents. Research in this area is already underway, and Arruda (2003) compared the adsorbent capacity of apple waste, rice husk, and natural sponge. Other studies, such as those by Reis, Oliveira and Rocha (2005) on the use of coffee husk and Silva *et al*. (2013) on green coconut fiber as heavy metal adsorbents, demonstrate the potential of different materials for this application.

In this sense, an example of an abundant raw material is coffee husk, which comes from the processing of coffee. By benefiting the coffee of the Acaiá variety, approximately 60 % of the husk is obtained by mass, while for the Mundo Novo variety this value is 53.4 %, and for the Catuaí variety, about 48.5 %. (SFREDO, 2006). The efficient exploitation of this agro-industrial by-product, especially in the Muzambinho region, as an adsorbent agent of dyes, such as NET, appears as a relevant contribution to the scientific advancement of the country and the development of sustainable technologies.

Most of the research related to the use of coffee husks has been carried out in Brazil. The use of agro-industrial waste in animal feed is already the object of study, aiming at reducing production costs. In this context, new research on the use of coffee husk, whether chemically modified or not, as a natural dye adsorbent, has shown promise for the technological and sustainable development of the country, especially in the Muzambinho region.

In view of the serious environmental problem, attributable to the indiscriminate disposal of effluents containing highly toxic dyes, such as eriochrome black T (NET), it is imperative to employ efficient technologies in the removal of these contaminants from aquatic environments. Thus, the objective was to evaluate the efficiency of the use of the residue obtained after the processing of coffee in the adsorption of eriochrome black T dye, dissolved in aqueous solution. Another objective evaluated in this experiment was the evaluation and verification of the potential use of chemical modification of coffee husk through acidification to provide improvements in the results obtained.

Material and methods

Obtaining and characterizing bioadsorbents obtained from coffee husk

The biomass chosen for this project was coffee husk, an agro-industrial residue from the processing of Arabica coffee from the city of Muzambinho. The coffee husk used in this study comes from a dry processing process. Therefore, no additional drying process was required. Moreover, the only process to which the coffee husk was submitted, before the experiments were carried out, was the grinding and extraction in soxhlet for the purification of the coffee husk (DA SILVA *et al.*, 2011). Part of the purified coffee husk (CC) was acidified with 0.1 mol^{L-1}HCl solution, wherein the system was maintained by constant stirring for 24 hours. After this procedure, the obtained product was filtered and washed with deionized water to neutral pH and designated as coffee husk that was subjected to the acidification process (CCA) (DA SILVA *et al.*, 2011).

Kinetic and equilibrium study on removal of NET dye in aqueous solution

The adsorption studies for the evaluation of bioadsorbents in the removal of NET dye from aqueous solutions were performed in triplicate and batch (DA SILVA, 2014). The amount and percentage of dye adsorbed by the adsorbents were calculated using Equations 1 and 2, respectively:

$$q = \frac{(C_o - C_f)}{m}.f \quad (1)$$

$$\%Remoção = 100.\frac{(C_o - C_f)}{C_o} \quad (2)$$

Where:
q = value of dye removed by the adsorbents (mg g^{-1}).
C_o = initial concentration of dye which is in contact with the adsorbent (mg L^{-1}).
C_f = final concentration of dye (mg L^{-1}) after the adsorption process.
m = mass of adsorbent (g).

The pseudo first order equation (Equation 3), pseudo second order equation (Equation 4), the general order equation (Equation 5) and intraparticle diffusion equation (Equation 6) were adopted to investigate the adsorption kinetics of the dyes removed by the bioadsorbents:

$$q_t = q_e[1 - exp(-k_1.t)] \quad (3)$$

$$q_t = q_e - \frac{q_e^2 k_2 t}{[k_2(q_e).t + 1]} \quad (4)$$

$$q_t = q_e - \frac{q_e}{\left[K_N.(q_e)^{n-1}.t.(n-1)+1\right]^{1/1-n}} \quad (5)$$

$$q_t = k_{id}\sqrt{t} + C \quad (6)$$

Where:
t represents the time in seconds; q_t represents the initial concentration of the adsorbed dye; q_e represents the equilibrium concentration of the adsorbed dye; K_N represents the rate constant; k_{id} represents the intraparticle diffusion rate constant; C represents a constant that is related to the thickness of the boundary layer; n is the general order; and k_1 and k_2 are constants (DA SILVA, 2014).

To evaluate the physicochemical parameters that were obtained, two mathematical isotherm models were used:

– Langmuir's isotherm model (LANGMUIR, 1918).

The mathematical expression for Langmuir's model is shown in Equation 7:

$$q_e = \frac{Q_{máx}.K_L.C_e}{1 + K_L.C_e} \quad (7)$$

Where:
q_e represents the adsorbed amount of adsorbate at equilibrium (mg g^{-1}); Q_{max} represents the maximum adsorption capacity of the adsorbent (mg g^{-1}); K_L represents the Langmuir equilibrium constant (L mg^{-1}); and C_e represents the equilibrium concentration of the dye (mg L^{-1}).

– Freundlich's isotherm model (FREUNDLICH, 1906).

Equation 8 is a mathematical expression for the Freundlich model:

$$q_e = K_F . C_e^{1/n_F} \quad (8)$$

Where:
K_F represents the Freundlich equilibrium constant [mg g^{-1} (mg L^{-1})$^{-1/nf}$]; ^{nf} is a dimensionless exponent of the Freundlich equation.

Results and discussion

The calibration curve obtained for the quantification of NET adsorbed by CC and CCA was adjusted according to the following equation: y = 0.011x - 0.0053, with r^2 in the value of 0.9991.

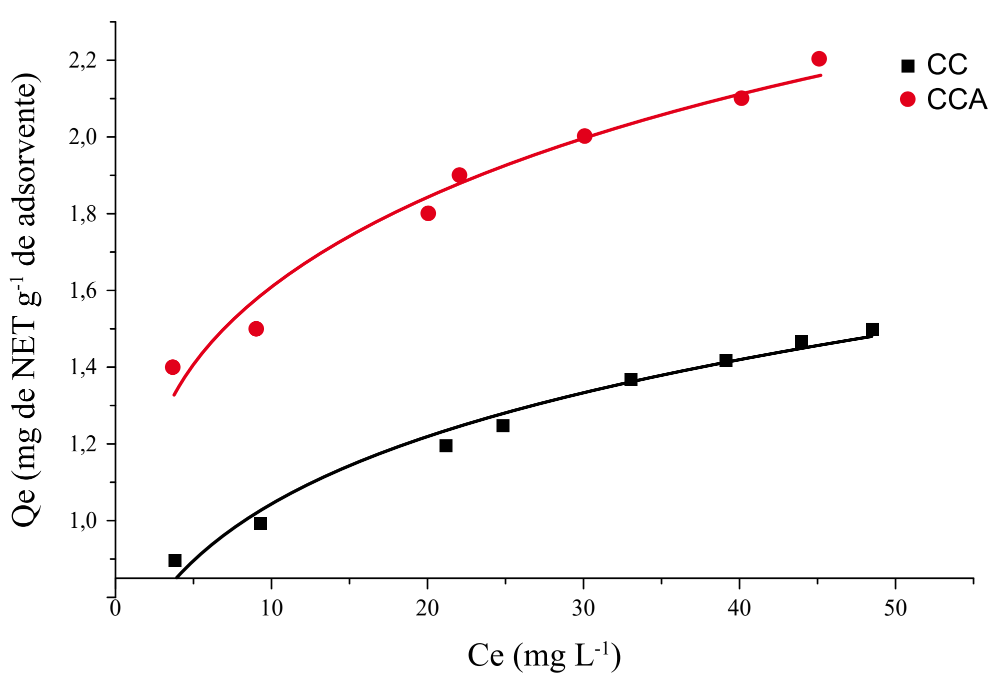
The adsorption isotherms, according to the Langmuir-Freundlich model, obtained after performing the experiments can be seen in Figure 2.

The parameters obtained after adjusting the results according to the Langmuir-Freundlich isotherm model are shown in Table 1. It is observed that the maximum amount of the adsorbed eriochrome T (net) black dye was respectively 483.9 mg ± 17.35 mg and 547.2 mg ± 22.98 mg for each gram of CC and CCA used in the adsorption process. These values are approximately nine times higher when compared to that obtained by the study by Dave, Kaur and Khosla (2011), who, when applying eucalyptus peel as an adsorbent agent for adsorption of the NET dye, obtained a Qm value of 52.32 mg g^{-1}, which shows the efficiency of CC and CCA as an adsorbent agent of the NET dye.

There is a greater adsorption capacity of CCA, that is, modifying the chemical structure of coffee fibers through acidification prior to the adsorption process forms a bioadsorbent that promotes greater adsorbent/adsorbate interaction in aqueous solution since the NET dye has anionic chemical structure (ALAMZEB *et al*., 2022).

The value of the constant n less than 1 for CC and CCA is indicative of the heterogeneity of the adsorption processes, while the values of $r^2$are proof that the results obtained fit adequately to the Langmuir-Freundlich isotherm model.

Figure 2. Adsorption isotherms according to the Langmuir-Freundlich model obtained after the experiments in Muzambinho – MG



Source: Prepared by the authors.

Table 1. Parameters obtained from the Langmuir-Freundlich isotherm of NET adsorption by CC and CCA

Isotherm	Parameters			
Langmuir-Freundlich	**Fibers**	**Qm(mg g^{-1})**	**n**	**r^2**
$Qe = Qm.\ Kl.\ C_e^n/1 + Kl.\ C_e^n$	CC	483.9 ± 17.35	0.2196	0.9731
	CCA	547.2 ± 22.98	0.1953	0.9564

Legend: In the formula, *Qe* represents the equilibrium concentration of the adsorbed dye; *Qm* represents the maximum adsorption capacity of the adsorbent ;and C_e represents the equilibrium concentration of the dye. CC is equivalent to coffee husk without being subjected to chemical treatments. CCA represents the coffee husk that has been subjected to the acidification process.

Calciolari *et al*. (2022) found the maximum adsorption capacity (Qm) of Coffee Silver Skin of 313.69 mg g^{-1}, for methylene blue dye. This result is superior to other low-cost materials used for this purpose, even though it is lower than those obtained in this work, analyzing the husk resulting from the coffee processing process, with or without chemical acidification. The coffee grounds also have high removal efficiency for safranin T dyes (Qm = 439.44 mg g^{-1}), malachite green (Qm = 1,328.53 mg g^{-1}) and dye mixture (Qm = 168.99), depending on the temperature used (QUITINO, 2021), which indicates the potential of using residues from coffee activity in the bioadsorption of molecules from textile dyes dissolved in aqueous solution.

Conclusions

The CC and CCA fibers were efficient as adsorbents for removal of NET in aqueous solution, since high adsorption capacity of the NET dye from aqueous solution was demonstrated by the coffee husk fibers, whether chemically modified or not. This is evident when the results obtained are compared with those found in the literature, which indicates a further application of this biomaterial in the treatment of wastewater contaminated with dyes.

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