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Use of nanostructured composite as biosorbent for removal of anionic dyes in water

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Abstract

The disposal of dyes in water bodies causes significant changes to the environment and is already among the hazardous chemicals with the potential to affect human health. Among the most popular methods of removing dyes and pigments from industrial waste, adsorption can be highlighted. The objective of this project was to evaluate the potential of nanomodified biomass of the *Cocus nucifera* species as a biosorbent for the removal of the anionic dyes erychrome black (EB), indigo blue (IB) and sulfur black (SB) in aqueous solution. The study revealed that the pHpzc of the nanocomposite is 5.1, that the sorption process is facilitated the lower the pH and that increasing the dose does not increase the sorption potential of the material. The kinetic study revealed that the theoretical mathematical model that best adjusted to the experimental data for the dyes EB, IB and SB was the pseudo-second order, with equilibrium being reached in 30, 50 and 90 minutes of contact time, respectively. The maximum adsorption capacity of the composite was 142.84, 162.76 and 106.32 mg/g for EB, IB and SB, respectively. The green coconut-based nanocomposite can be used as an efficient biosorbent to treat dye-contaminated water.

Keywords: Green coconut; Sorption, Eriochrome black; Indigo blue; Sulfur black.

1. Introduction

The disposal of dyes in water bodies causes significant changes to the environment and is already among the hazardous chemicals with the potential to affect human health. Due to their complex structure and because they are not photodegradable, remain soluble at high temperatures and are not sensitive to microbiological attack, most dyes are persistent in the environment. In addition, most azo dyes are toxic to the aquatic environment, in addition to being carcinogenic and mutagenic [1, 2]. Synthetic organic dyes are classified into different categories according to their chemical structures such as azo, anthraquinone, nitro, acridine and sulfur dyes[3, 4].

Among the most popular methods of removing dyes and pigments from industrial waste, adsorption can be highlighted. The types of materials used as adsorbents are of various natures, and can be of plant origin, such as peat and cellulose derivatives, of animal origin, such as eggshell membranes, or of synthetic origin, such as alumina, sepiolite and others [5].

The green coconut biomass can be an alternative adsorbent source for dye sorption, as it is an abundant biomass, especially in the northeast, has good productivity and does not require replanting. Therefore, the objective of this project was to evaluate the potential of nanomodified biomass of the *Cocus nucifera* (BCNP) species as a biosorbent for the removal of the anionic dyes erychrome black (EB), indigo blue (IB) and sulfur black (SB) in aqueous solution.

1 Materials and methods

1.1 Preparation of magnetite nanocomposites

The nanomodified biomass was obtained from the methodology proposed by Labuto et al., (2022).

1.2 Adsorption assays

To determine the point the zero charge (pH_{PZC}), the methodology proposed by Carvalho et al., (2021) was applied. For this, 50 mg of the bamboo adsorbent, 25mL of 1 mol/L sodium chloride solution, at 2-12 pH range, were used. The system was kept in constant agitation (200 RPM) in a shaker-type incubator, temperature (28 ºC) for 24 h, after which, the final pH of each solution was measured.

The effect of pH in the range between 3 and 5 was evaluated, using 10 mg of analyte for each 10 mL of dye solution (IB, EB and SB 100 mg/L).

The kinetic study was continuous at constant pH (pH 3.5) using 10 mL of EB, IB and SB solution (concentration 100 mg/L) and 10 mg of BC-NP. During the test, aliquots were collected at intervals of 5, 10, 15, 30, 60, 120 and 180 minutes.

The dosage effect was evaluated from the use of 10 to 50 mg of biocomposite (BCNP) for each dye (IB, SB and EB 100 mg/L), pH 3.5 and 60 min.

For the adsorption isotherm, 10 mL of IB, SB and EB (50 to 350 mg/L) synthetic solutions were used at pH 4.0. The experiment was conducted using 10 mg of adsorbent for every 10 mL of solution.

The analysis conditions were: constant agitation (200 RPM) in a shaker-type incubator, temperature (28 ºC), and 1 h interval. To determine the adsorption potential the solutions were centrifuged and the supernatant analyzed for dye quantification by UV-VIS spectrophotometry. The material particle size was between 48 and 100 mesh.

2 Results and discussion

The pH study revealed that the sorption process is facilitated at lower pH. For this reason, it was decided to work with pH 3.5, Figure 1b. The study of the adsorption kinetics revealed that the theoretical mathematical model that best adjusted to the experimental data for the dyes EB ($r^2 = 0.99963$), IB ($r^2 = 0.99905$) and SB ($r^2 = 0.99673$) was the pseudo-second order, with equilibrium being reached in 30, 50 and 90 minutes of contact time, respectively, as can be seen in Table 1 and Figure 1c.

Table 1. Data of pseudo-first and pseudo-second order kinetics by nanomodified biomass coconut (BCNP); For pseudofirst order, the slope = K_1, and the angular parameter = K_2 in the pseudo-second-order. Using 1 mg/mL biosorbent dose and 10 mL of solution, an initial concentration of 100 mg/L.

Dye	Pseudo 1st order				
	r^2	χ^2	K_1 (min^{-1})	$Q_{calc.}$ ($mg\ g^{-1}$)	$Q_{exp.}$ ($mg\ g^{-1}$)
EB	0.8433	0.0845	-0.01 ± 1.7^{-3}	49.50	55.50
IB	0.87749	0.10798	0-.05 ± 1.7^{-4}	16.30	49.90
SB	0.19004	1.98311	-0.01 ± 3.1^{-4}	13.51	62.31
	Pseudo 2nd order				
Dye	r^2	χ^2	K_2 (min^{-1})	$Q_{calc.}$ ($mg\ g^{-1}$)	$Q_{exp.}$ ($mg\ g^{-1}$)
EB	0.99963	0.00043	0.01±$5.^{-3}$	59.31	55.50
IB	0.99905	0.00132	0.01±5.0^{-3}	48.64	49.90
SB	0.99673	0.00307	0.01 ± 3.1^{-4}	60.47	62.31

During the studies of the influence of the dye concentration, it was possible to observe that the maximum adsorption capacity of the composite was 142.84, 162.76 and 106.32 mg/g for EB, IB and SB, respectively, Figure 1a.

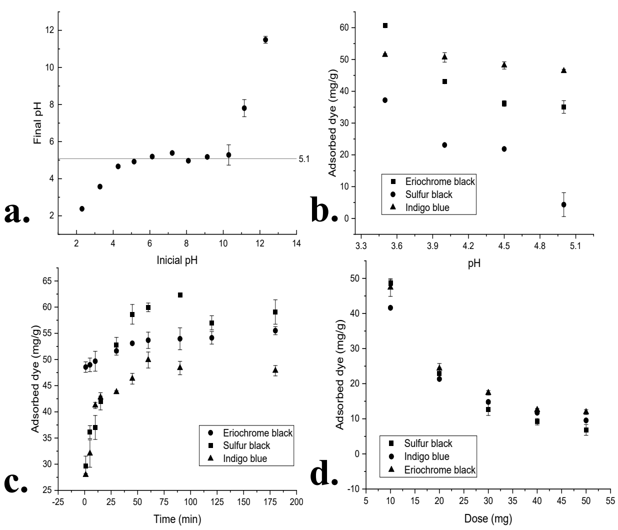

Figure 1. Study of the point of zero charge (pHPZC) for biocomposite (**a**); effect of pH (**b**) and dosage (**d**); study of adsorption kinetics (**c**). Sorption study of eriochrome black (EB), indigo blue (IB) and sulfur black (SB) dyes using 10 ml of solution and concentration of 100mg/L, n=3.

The results show that dye sorption increases as the dose increases. However, sorption capacity (Q_e) decreases with increasing dose for all dyes. For this reason, it was decided to work with the lowest dose (1mg/mL), Figure 1d.

The isothermal studies indicate that the Langmuir (r^2 0.98444) and Freundlich (r^2 0.99042) models had a better fit to the experimental data in EB sorption, Figure 2b. In IB sorption, the models that provided the best fit were Langmuir (r^2 0.96061) and Temkin (r^2 0.96532), Figure 2c. In the SB study, Langmuir (r^2 0.92104) and Freundlich (r^2 0.95183) provided the best fit to the experimental data, as can be seen in Figure 2d and Table 2.

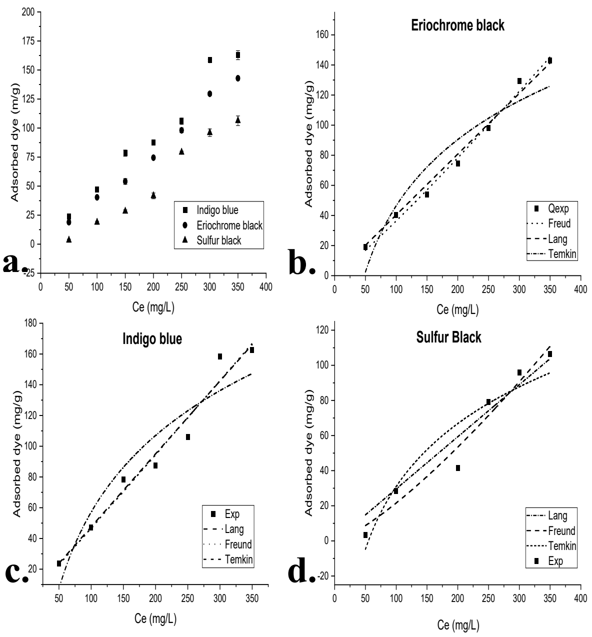

Figure 2. Adsorption isotherm of dyes by the biocomposite (**a**). Experimental curves for Langmuir, Freundlich and Temkin isotherms models fitting to for eriochrome black (**b**) indigo blue (**c**) and sulfur black (**d**) sorption using 10 ml of solution and dose of 10 mg, pH 3.5 and n=3.

Langmuir isotherm is characterized adsorption occurs homogeneously and, in a monolayer, forming sites of equal energy and without interactions between the adsorbed molecules [8]. Freundlich isotherm model considers the heterogeneous adsorption process, which occurs in multilayers, and the active adsorption sites have different energy values (Debnath & Das, 2023).

Table 2. Data of experimental sorption capacity (Q_{exp}), isotherm parameters, and χ^2 error evaluation for Eriochrome black (EB), indigo blue (IB) and (SB) sorption by MS-NP (nanomodified mesocarp). SD = standard deviation; SE = standard error provided by fitting the model to the experimental data. n = 3.

	EB	IB	SB
Q_{exp} (mg/g)	142.84 ± 6.56 (SD)	162.76 ± 7.9(SD)	106.32 ± 1.98(SD)
Langmuir			
Q_{max}	141038 ± 1.6 7(SE)	51219 ± 2.8^{6}(SE)	190576 ± 1.27^{8}(SE)
b (L/g)	2.86^{-6} ± 3.3^{-4}(SE)	9.3^{-6}± 5.17^{-4}(SE)	1.55^{-6} ± 0.001(SE)
χ^2	33.02	107.8	131.83
r^2	0.98444	0.96061	0.92104
Freundlich			
Kf (mg/g) (L/mg)/n	0.904 ± 0.051(SE)	0.02 ± 0.0057(SE)	0.053 ± 0.066(SE)
nf	0.904 ± 0.051SE)	0.31 ± 2.67^{6}(SE)	0.76 ± 0.13(SE)
χ^2	20.32	462	80.42
r^2	0.99042	0.83132	0.95183
Temkin			
b_T	0.3401 ± 2.9^{6}(SE)	345 ± 32.85(SE)	0.39 (SE)
K (L/mg)	0.02079 ± 5.1^{-3}(SE)	2.17 ± 0.95(SE)	0.018 ± 0.005(SE)
X^2	0.89017	3.06	296.69
r^2	0.83526	0.96532	0.8223

3 Conclusion

Due to the results presented, green coconut-based nanocomposite can be used as an efficient biosorbent to treat dye-contaminated water, it is a promising technology. Furthermore, the magnetization of the green coconut biomass facilitated the removal of the adsorbent complexed with the contaminants dispersed in solution through the application of an electromagnetic field.

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