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Comparative study of adsorption of Remazol Black onto PAni@Fe_2O_3 and PAni@Fe_3O_4

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Abstract

The aim of this work was a preliminary comparative analysis of the adsorptive capacities of polyaniline-based composites (PAni@Fe_2O_3 and PAni@Fe_3O_4) for the removal of the synthetic organic dye Remazol Black (RB) in aqueous solution. The composites were characterized by XRD and BET to evaluate their structural and textural properties. Experimental data revealed that both composites have an efficiency of removal of 98%. The Langmuir-Freundlich and Sips isotherm models best fitted equilibrium data, suggesting a heterogeneous adsorption mechanism. The findings imply that both composites have potential as effective adsorbents for removing of recalcitrant organic dyes from wastewater.

Keywords: polyaniline, dye removal, composites;

1. Introduction

Pollution of water bodies remains a significant environmental challenge, with synthetic organic dyes among the most toxic contaminants. These dyes, used in industries such as textiles, pharmaceuticals, cosmetics, and food, are resistant to conventional effluent treatment methods due to their recalcitrant nature [1]. Consequently, developing efficient technologies to address this issue is crucial.

Recently, there has been progress in developing efficient adsorbents based on polymers, including composites and blends. Polyaniline (PAni) is an intrinsically conductive polymer that has gained attention from the scientific community due to its properties such as surface area, stability, and ease of synthesis. When used as the base of a composite, its adsorptive capacity can be increased, improving removal efficiency [2,3] and addressing the previously mentioned challenge.

Among the materials used to enhance the properties of PAni as an adsorbent, hematite (iron oxide - Fe_2O_3) is notable for its reactivity, which can enhance the overall efficiency of the composite in capturing molecules [2]. Magnetite (Fe_3O_4), with its magnetic properties, low toxicity, and easy recovery, is another promising material. However, its disadvantages include low stability and molecule aggregation, which hinders its application in aqueous waste remediation [4]. To overcome these limitations, incorporating these oxides into composites increases their applicability and potentially improves the performance of engineered adsorbents compared to traditional adsorbents.

Therefore, the objective of this work is to conduct a preliminary comparative study of the adsorptive capacity of PAni@Fe_2O_3 (hematite) and PAni@Fe_3O (magnetite) composites, using the synthetic organic dye Remazol Black (RB) as the model adsorbed molecule. Both composites were synthesized, characterized, and subjected to batch adsorption tests, evaluating parameters such as adsorbent dosage and initial dye solution concentration. Additionally, adsorption equilibria were assessed.

2. Methods

PAni: The composite was synthesized by the chemical oxidation of aniline, using a method adapted from the research group [5]. The molar ratio used was aniline 1: HCl 4: APS 1.25. Aniline (Sigma Aldrich) and HCl (Vetec) were stirred for 30 minutes until the reaction temperature (10°C) was reached. Then, an aqueous solution of ammonium persulfate - APS (Dinâmica) was added dropwise. The reaction was conducted for 4 hours. The reaction mixture was left to rest for 12 hours, then filtered and washed with distilled H_2O and ethanol P.A. (Proc9). Finally, it was dried in an oven (Odontobrás) at 80°C for 24 hours.

PAni@Fe_2O: One-pot synthesis was performed using the same procedure described above, with a molar ratio of aniline 1: HCl 4: APS 1.25: Fe_2O_3 0.5, where Fe_2O_3 (Sigma-Aldrich) was added initially along with aniline and HCl.

PAni@Fe_3O_4: Using a method adapted from Long *et al.* [6], the composite was prepared by dispersing 3.0 g of PAni in a Fe^{3+}/Fe^{2+} solution (7.5 mmol/6.25 mmol) at 80°C under vigorous stirring for 1 hour. The reaction carried for 1 hour, and the pH was monitored and maintained between 11-12 by adding concentrated NH_4OH (Vetec). After the reaction, the solid was centrifuged, washed with distilled H_2O and ethanol P.A., and dried in an oven at 80°C for 24 hours.

For both composites, after preparation, the material was doped with a 0.1 M HCl solution for 1 hour.

Characterization: The starting materials (PAni, Fe_2O_3, and Fe_3O_4) and the prepared composites were characterized by XRD and BET.

Adsorptive Study: For the adsorptive study, the synthetic organic dye (RB) (DyStar) was used as the model molecule in an aqueous solution. For both composites, studies were conducted to assess the effect of adsorbent dosage (0.5 - 2 g L^{-1}) and initial dye concentration (20 - 100 mg L^{-1}). Batch experiments were carried out for 90 minutes at room temperature (25°C) and the natural pH of the solution, which is approximately 5.5. The final concentration of the adsorption tests was determined by UV-vis spectroscopy (Varian, Cary 50). Additionally, adsorption equilibrium studies were performed.

3. Results and discussion

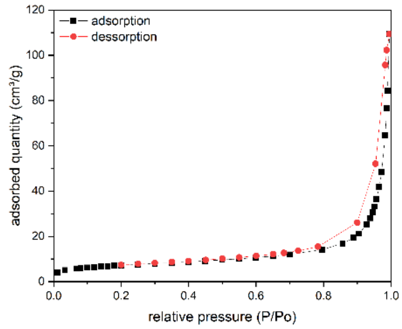
The textural properties of the synthesized composite were evaluated using the BET technique, with the results shown in Table 1. An increase in the surface area was observed for both composites (with ferrite and magnetite) when compared to PAni as a reference. For PAni@Fe_2O_3, this increase was 10.1%, while for PAni@Fe_3O_4, it was 49%, giving this composite a higher probability of adsorbing molecules on its surface. The increase in surface area in both composites is likely due to the incorporation of a second material into the PAni structure. Regarding pore volume, although there was an increase of 16% for PAni@Fe_2O_3 and 42% for PAni@Fe3O4, the pore volume remained within the same order of magnitude. According to the results shown in Fig. 1, the isotherm is of type II, characteristic of mesoporous materials.

Table 1. Properties of the textural analysis.

Sample	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
PAni	23,48	0,12
Fe_2O_3	8,19	0,00*
Fe_3O_4	72,50	0,00*
PAni@Fe_2O_3	25,87	0,15
PAni@Fe_3O_4	34,99	0,14

* Lower than < 0,0001 $cm^3.g^{-1}$.

(a)



(b)

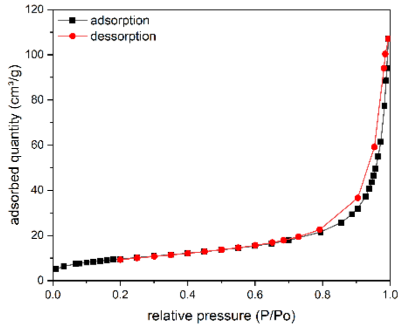


Fig. 1. N_2 isotherm of (a) PAni@Fe_2O_3 and (b) PAni@Fe_3O_4.

The diffraction patterns of the starting materials (PAni, Fe_2O_3, Fe_3O_4) and the composites (PAni@Fe_2O_3 and PAni@Fe_3O_4) are shown in Fig. 2. The XRD pattern of PAni@Fe_2O_3 (Fig. 2a) displays a low-intensity diffraction band characteristic of PAni at 25.40°, revealing its amorphous nature. The shift in comparison to the same band in the pure PAni sample indicates a chemical association between Fe_2O_3 and the polymer [2]. The other crystalline peaks (24.07°, 33.18°, 35.59°, 40.86°, 54.02°, 57.51°, 62.42°, 63.95°, 71.88°, 75.53°) correspond to the planes of Fe2O3 [7]. In contrast, the XRD pattern of PAni@Fe_3O_4 (Fig. 2b) shows the characteristic PAni band with higher intensity compared to PAni@Fe_2O_3, which can be attributed to a greater orientation of the PAni chains [4]. The other crystalline peaks (30.23°, 35.49°, 43.26°, 53.66°, 57.20°, 62.83°, and 74.39°) correspond to the planes of cubic inverse spinel Fe_3O_4 [8].

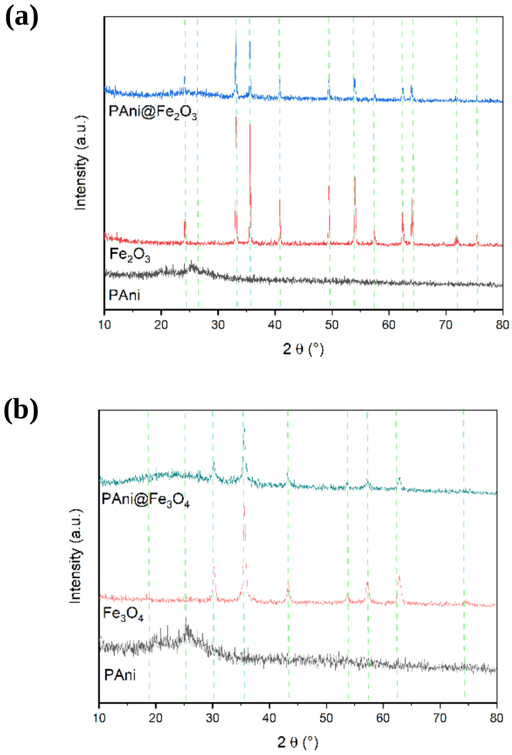


Fig. 2. XDR of (a) PAni@Fe_2O_3 and (b) PAni@Fe_3O_4.

Fig. 3 shows the results of the adsorbent dosage study for the adsorption of RB dye. This test was conducted with an initial dye concentration of 20 mg L^{-1}. It was observed that with 1 g L^{-1}, a removal efficiency greater than 95% was achieved for both composites, indicating this as the optimal adsorbent dosage.

The study of the effect of initial adsorbent concentration (Fig. 4) revealed the same trend for both adsorbents: the lower the initial dye concentration in the aqueous solution, the higher the removal efficiency, reaching 98% removal at 20 mg L^{-1} for both adsorbents. This behavior can be attributed to the fact that the active sites of the adsorbent become saturated more quickly with higher dye concentrations in the solution, making it difficult for the dye molecules to access the active sites on the adsorbent's surface.

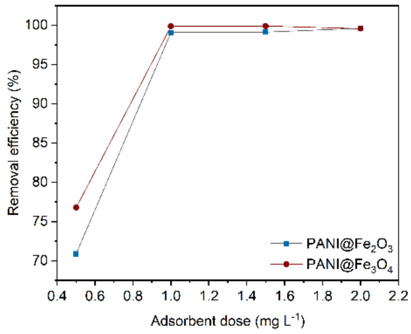


Fig. 3. Effect of the dosage of the adsorbent on the removal of dye.

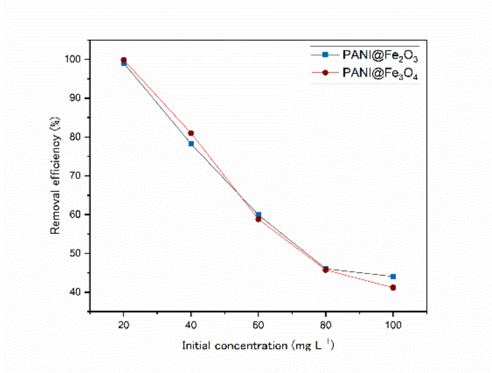


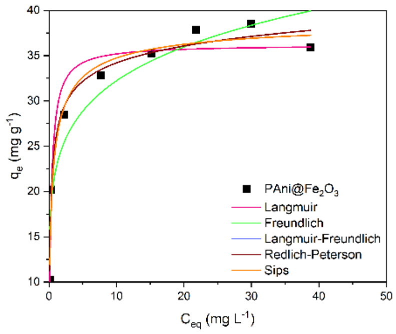
Fig. 4. Effect of the concentration of the adsorbent on the removal of dye.

For dye concentrations greater than 40 mg L^{-1}, PAni@Fe_3O_4 achieved slightly better removal efficiencies for RB. This result is consistent with the textural properties (Table 1), where PAni@Fe_3O_4 has a higher surface area than PAni@Fe_2O_3, indicating more active sites for dye adsorption, thus taking longer to reach saturation.

Non-linear isotherm models (Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson, and Sips) were evaluated for the experimental data, with the results shown in Fig. 5. For PAni@Fe_2O_3 (Fig. 5a), the Langmuir-Freundlich (q_{max} = 33.43 mg g^{-1}, R^2 = 0.96) and Sips (q_{max} = 33.43 mg g^{-1}, R^2 = 0.96) models provided the best fit, with other models showing fits ranging from 0.82 to 0.93. For PAni@Fe_3O_4 (Fig. 5b), the Redlich-Peterson model provided the best fit (R^2 = 0.98), followed by the Langmuir-Freundlich (q_{max} = 39.34 mg g^{-1}, R^2 = 0.97) and Sips (q_{max} = 39.33 mg

g^{-1}, $R^2 = 0.97$) models, while other models had R^2 values around 0.90. These results suggest that at low concentrations, adsorption on the composites follows the Freundlich model, while at higher concentrations, it follows the monolayer model [9].

(a)



(b)

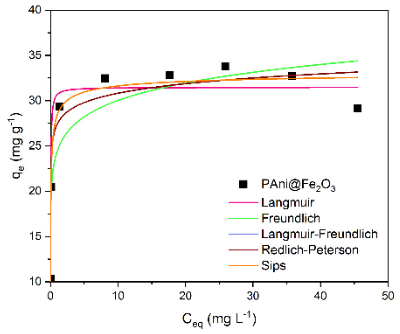


Fig. 7. Isotherms of adsorption of RB on (a) PAni@Fe_2O_3 and (b) PAni@Fe_3O_4, using a contact time of 4h.

Higher n values indicate a greater binding affinity between the adsorbate and the adsorbent [3]. Thus, comparing the n values of the Langmuir-Freundlich models for PAni@Fe_2O_3 (n = 1.5) and PAni@Fe_3O_4 (n = 2), a higher affinity of the dye with PAni@Fe_3O_4 is observed.

4. Conclusion

The XRD results confirmed the incorporation of oxides into the composites. BET results showed that PAni@Fe_3O_4 has a larger surface area compared to PAni@Fe_2O_3, which can be associated with better removal efficiency. The adsorption study demonstrated that both composites were efficient in removing Remazol Black dye from aqueous solution under the conditions studied, highlighting their potential for use in environmental pollutant removal.

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