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Effects of organic and inorganic additives on the development of structured adsorbents for textile effluent treatment applications

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Abstract

Adsorbents are often used in the form of powders or pellets. However, previous studies have shown that impregnating these materials in structures facilitates both the adsorption process and the regeneration of the adsorbent. In order to reach this goal, it is necessary to develop solutions that promote stability and rheological behavior, in addition to improving the properties of the adsorbent. Considering the need to treat effluents and the advantages of impregnating adsorbents in structures, this study aims to formulate a suspension containing the adsorbent commercial activated carbon (C1012), with percentages of polyvinyl alcohol (PVA) and zinc oxide nanoparticles (ZnONPs) for impregnation in metal structures to remove textile dyes. Five suspension solutions were prepared following a 2^2 factorial statistical design. The analysis revealed that the addition of PVA and ZnONPs affected both Sa and q of the adsorbents. The Sa of the suspensions decreased by approximately 15% compared to C1012 in natura (1258 $m^2 \cdot g^{-1}$), with Sa values ranging from 1057 to 1181 $m^2 \cdot g^{-1}$. The suspensions with 7% PVA and 5% ZnONPs (AD-M3) exhibited the highest Sa (1181 $m^2 \cdot g^{-1}$) and Pd (1.84 nm). The adsorption capacity (q) of the adsorbents was reduced but remained at an efficient level, with AD-M2 (3% PVA and 5% ZnONPs) achieving the highest q (4.01 $mg \cdot g^{-1}$). Higher percentages of PVA and ZnONPs resulted in lower q values, whereas moderate percentages (3-5%) keeps Sa and q. It was concluded that a suspension containing 7% PVA and 5% ZnONPs exhibited the best overall performance in adsorption and adsorbent structuring.

Keywords: activated carbon; textile dye; batch adsorption; PVA; ZnONPs.

1. Main text

Textile industries generate large quantities of dye-containing effluents. Due to their nature, it is necessary to apply treatments capable of degrading and/or removing textile dyes [1]. Adsorption is an additional effluent treatment method that is becoming increasingly attractive due to its proven effectiveness in removing dissolved dyes, as well as the possibility of recycling materials as adsorbents [2].

Adsorbents are generally used in powder form; however, the technique of impregnating them into structures based on metal alloys, ceramic materials, and even plastic materials is increasingly being used [3]. To achieve this, suspensions are made containing a diluent, adsorbent, and additives that promote the adhesion of the adsorbent to the structure. Polyvinyl alcohol (PVA) is an organic polymer widely used as an additive in various industries [4]. Zinc oxide nanoparticles (ZnONPs) are widely used in industry [5]. These additives improve the performance of suspensions by promoting their stability and rheological behavior and improving the efficiency of structured adsorbents [6]. However, the presence of additives can interfere with the structure and adsorption capacity of the adsorbent [7].

Therefore, it is necessary to study the properties before and after the application of additives to define the optimal percentage of additives in suspension solutions containing an adsorbent for coating structures. Therefore, the aim of this research was to determine the optimal percentage of PVA and ZnONPs to prepare a suspension of commercial activated carbon for the subsequent production of structured adsorbents. To this end, a factorial statistical design study was carried out to analyze the effects of the additives on the properties of the adsorbent.

2. Materials and Methods

The study of adsorbent structures involves coating substrates with suspensions containing the adsorbent and additives. Before coating structures are formed, it is essential to define a suspension that is compatible with the substrate and that maintains its adsorbent properties. In this study, five different

suspensions were studied in which the percentages of the PVA additive and ZnONPs were varied.

2.1 Preparation of suspensions

75g suspension was prepared using 15% solids by weight at an additive/adsorbent mass ratio. Distilled water with a pH of 4 was used as the solvent owing to the zero charge point (ZCP) of the solid [8] and the commercial activated carbon adsorbent C1012 (brand: Labsynth), whose ZCP is 7.4. PVA P.S. - $(C_2H_4O)_n$ (Dinâmica, Química contemporânea Ltda, Brazil) and ZnONPs (Nyacol DP5370) were used as additives. The additive percentages were defined using a 2^2 factorial design with a central point in triplicate. This was also used to evaluate the adsorption capacity of the suspensions and the effect of the additives on the specific surface area (Sa). The planning matrix is shown in Table 1.

Table 1. Fatorial design matrix 2^2

Adsorbent	PVA	ZnONPs
AD-M1	1 (7%)	1 (15%)
AD-M2	-1 (3%)	-1 (5%)
AD-M3	1 (7%)	-1 (5%)
AD-M4	-1 (3%)	1 (15%)
AD-M5	0 (5%)	0 (10%)
AD-M5	0 (5%)	0 (10%)
AD-M5	0 (5%)	0 (10%)

*AD, Adsorbent; M- modified

The pH of the solvent was adjusted using 1 $mol \cdot L^{-1}$ nitric acid and heated to 80°C. The adsorbent was then gradually added under agitation and interspersed with ultrasound treatment for 15 min [8]. Finally, Nyacol was added. The suspension was stirred for 24 h. When the suspensions were ready, they were calcined for 4 h in a muffle furnace at 250°C to remove all the existing moisture. In this way, each suspension can be referred to as a modified adsorbent, following the respective numbering adopted in the planning matrix shown in Table 1.

2.2 Characterization of the adsorbents and study of the adsorption of textile dyes.

The Sa was determined by the adsorption/desorption of N_2 at 77 ± 5 K using the Brunauer, Emmett, Teller (BET) method (BELSORP-MINI from Bel Japan Inc). Pore diameter (Pd) and pore volume (Pv) were determined using the Barrett, Joyner, Halenda (BJH) method. The adsorption capacity of each material was evaluated by performing batch tests. This was carried out with each adsorbent C1012 (brand: Labsynth) following the methodology of [9], in which 25 mL of dye solution at 25 ppm, at natural pH, and 0.1 g of adsorbent were added to a 125 mL erlenmeyer flask, and the solution was left to stir at 300 rpm on a shaking table (IKA KS130 control) for 2 h at room temperature (28±1°C). After this period, the dye solution with the adsorbent was filtered through blue filter paper (90±1mm) and then centrifuged (model Q222T216, QUIMIS) for 10 min at 10 rpm. Dye removal was assessed using absorbance in a UV/Vis spectrophotometer. It is possible to quantitatively define the removal using Equation 1.

$$q = \frac{(C_0 - C_f) * V}{m} \quad (1)$$

where q is the adsorptive capacity ($mg \cdot g^{-1}$); C_0 and C_f are the initial and final dye concentrations ($mg \cdot L^{-1}$), respectively; V is the volume of the solution (L), and m is the mass of the adsorbent (g) [10]. The adsorption study was conducted with monocomponent solution. Dye was studied the anionic dye direct blue 71 (AD71).

The effects of adding additives on q and Sa were evaluated using the Minitab statistical 19 software.

3. Discussions and results

3.1 Characterization of the adsorbents

N_2 adsorption and desorption isotherms (not shown in this article) were used to obtain the porosity data of the adsorbents. The porosity data, surface characteristics of the materials, adsorption capacity (q), and adsorption efficiency (Ef) are listed in Table 2. Table 2 lists the values for the characteristics of C1012 and the adsorbents in the suspension solutions.

Table 2. Characteristics of the adsorbents.

	C 1012	AD-M1	AD-M2	AD-M3	AD-M4	AD-M5
Sa ($m^2 \cdot g^{-1}$)	1258	1064	1173	1181	1136	1057
Pd(nm)	1.68	1.76	1.68	1.84	1.76	1.61
Pv ($cm^3 \cdot g^{-1}$)	0.40	0.34	0.37	0.37	0.37	0.34
q ($mg \cdot g^{-1}$)	4.04	3.44	4.01	3.47	3.45	3.41
E_f (%)	97	95.5	96.5	95.7	96.2	94.7

The Sa values of the five suspensions were lower than the Sa of C1012 in natura, but no significant variation was observed. It can be seen that the AD-M1 and AD-M5 adsorbents formed by suspensions containing 7% PVA and 15% ZnONPs and 5% PVA and 10% ZnONPs, respectively, had the lowest Sa values of 1064 and 1057 $m^2 \cdot g^{-1}$. The increased percentage of PVA may have affected the adsorbent surface area. According to [11], polymeric adsorbents have lower Sa than natural adsorbents such as activated carbon and zeolites. This is because the added PVA was not completely removed during the calcination process; for it to be removed, it would have to be heated to 400 °C for 2 h [8]. However, the autoignition temperature of C1012 was 450 °C, implying that PVA remained in the adsorbent. The Pd values were in the 1.6 - 1.8 nm range, in which case the adsorbents were classified as microporous [12]. Adsorbent AD-M3 had the largest pore diameter (1.84 nm) and highest Sa values, and its Pv was higher than those of adsorbents 1 and 5. Higher Sa, Pd, and Pv ratios allow a large amount of the adsorbate to diffuse into the adsorbent, as well as helping to recycle it [7]. Considering these three characteristics, adsorbent AD-M3 stands out because it did not considerably reduce Sa and Pv but increased Pd due to the addition of PVA.

3.2 Effect of PVA and ZnONPs on the adsorption capacity and surface area of the adsorbent.

Batch adsorption tests were performed on the monocomponent dye solution (Table 2). The adsorption capacity efficiency of the five suspensions exceeded 95%. Adsorbent AD-M2, which contained 3% PVA and 5% ZnONPs, exhibited the highest efficiency (96.5%). The effects of adding additives on the adsorption capacity and surface area of the adsorbents are shown in contour graphs in Figure 2.

Figure 2 (A) shows that the adsorption capacity tended to decrease with increasing percentage of the additives. From 5% PVA and 10% ZnONPs, the value of q decreases to below 3.5 $mg \cdot g^{-1}$. On the other hand, when the percentages of PVA and ZnONPs were the lowest 3% and 5% respectively, the q increased (> 4 $mg \cdot g^{-1}$).

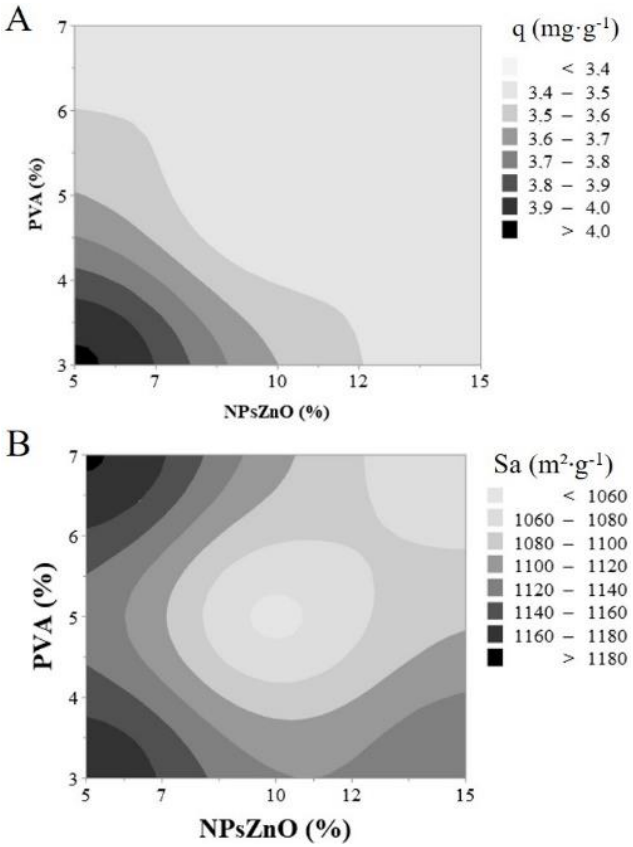

Fig. 2 Contour surface plot of (A) adsorption capacity and (B) Sa of each adsorbent in relation to the percentages of PVA and ZnONPs. Source: Autor, 2024

Unlike the adsorption efficiency, the additives interfered with the adsorption capacity. In a study by [11], PVA was found to increase the adsorption properties of chitosan, which can be attributed to the presence of hydroxyl functional groups (-OH) in greater content. However, the decomposition of ZnONPs can reduce q due to excess OH [13]. C1012 also has hydroxyl groups in its structure, which may have increased when PVA was added, explaining

why q decreased as the percentage of PVA and ZnONPs increased.

The graph in Figure 2 B shows the behavior of the surface area of the adsorbents in relation to the percentage of additives, PVA and ZnONPs. It can be seen that as the percentage of PVA increases to 7% and the percentage of ZnONPs is kept at 5%, the Sa increases and can be greater than 1180 $m^2 \cdot g^{-1}$. However, when the percentage of PVA (5%) and ZnONPs (10%) was increased, Sa decreased to less than 1060 $m^2 \cdot g^{-1}$. Continuously increasing the percentage of additives to 7% PVA and 15% ZnONPs also caused a reduction in the As of the adsorbent to approximately 1060-1080 $m^2 \cdot g^{-1}$. According to [7], the addition of PVA limits the surface area of the adsorbent. However, the limiting factor was the high percentage of ZnONPs.

4. Conclusion

The results show that the addition of the additives, PVA and ZnONPs, to suspension solutions containing the C1012 adsorbent did not affect the removal efficiency of the AD71 textile dye. There was a reduction in Sa, Pv and q, but these reductions were not significant. It also did not affect the Pd of adsorbents AD-M1, AD-M2, AD-M3 and AD-M4. As discussed, based on the analyses carried out, AD-M3, obtained from the suspension containing 7% PVA and 5% ZnONPs, was the best performing of the suspensions studied.

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