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Modification of commercial activated carbon: removal of cationic and anionic dyes, chromium(VI) and mercury(II)

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Abstract

Activated carbon is a well-known and versatile adsorbent widely used in the environmental field. With the urgency to improve water and effluent treatment technologies to remove pollutants, such as heavy metals, it is essential to develop simple technologies, such as the modification of activated carbon. Modifications to commercial activated carbon (CAC) aim to alter its texture, thus increasing its adsorptive capacity for certain compounds. In this context, the objective of this work was to test two modifications of CAC, using Nitric Acid (HNO_3) and Ammonium Hydroxide (NH_4OH) for adsorption of the dyes Methylene Blue and Methyl Orange and subsequently the heavy metals chromium(VI) and mercury(II). After the modifications, Surface Modified Activated Carbons (SMAC) that obtained better results in dye adsorption were subjected to surface characterization by nitrogen adsorption (BET), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). These SMACs were then tested for adsorption of mercury(II) and chromium(VI). The SMACs using NH_4OH and HNO_3 showed different effects on their adsorption properties, considerably improving the capacity and selectivity, especially for Methylene Blue and chromium(VI). The results obtained in this study indicate that these Surface Modified Activated Carbons are promising materials for use in water and wastewater treatment. Thus, this work contributes to the advancement of the area of treatment and removal of contaminants via adsorption, in search of simple and sustainable technologies.

Keywords: surface modified activated carbon; heavy metals; dyes; adsorption of pollutants.

1. Introduction

Activated carbon is a well-known and relevant adsorbent for the environmental area, especially important for the treatment of water and wastewater [1,2].

With the presence of various pollutants, heavy metals and the emergence of new contaminants, it is essential to develop new technologies and optimize the use of activated carbon [3]. This material is subject to modifications, which allow it to increase its adsorption power for metals and dyes, for example [4].

Current research focuses on modifying activated carbon to improve its adsorption efficiency and selectivity. Chemical modifications using agents like Nitric Acid (HNO_3) and Ammonium Hydroxide (NH_4OH) have shown promise in altering surface properties and introducing functional groups that interact more effectively with specific contaminants [3].

Despite these advancements, gaps remain in optimizing activated carbon for a broader range of contaminants and achieving higher adsorption capacities [5].

Thus, the objective of this work was to test two modifications of commercial activated carbon (CAC) using Nitric Acid (HNO_3) and Ammonium Hydroxide (NH_4OH) for adsorption of the dyes Methylene Blue (MB) and Methyl Orange (MO) and the metals chromium(VI) and mercury(II).

By investigating the enhanced adsorption capacities of modified CAC for both dyes and heavy metals, this study seeks to provide a deeper understanding of how chemical treatments can optimize activated carbon. The findings could contribute to developing more effective and sustainable water and wastewater treatment processes, addressing both current and future environmental challenges.

2. Materials e Methods

The reactional conditions for the surface chemical modifications of de CAC were optimized in a previous work using a Central Composite Rotational Design (CCRD). Each sample of around 10,0 g of CAC to a certain contact time and concentration of HNO_3 and NH_4OH (Table 01). Afterwards, the Surface Modified Activated Carbons (SMAC) were washed with distilled water and left to rest.

For adsorption tests, 0.2 g of each SMAC sample and 40 ml of each solution were used with the following concentrations:

Methylene blue: 250 mg · L^{-1};
Methyl orange: 50 mg · L^{-1};
Mercury chloride: 5 mg · L^{-1};
Potassium chromate: 5 mg · L^{-1}.

Each sample was stirred at 120 rpm for 24 h for subsequent reading on a UV-Vis spectrophotometer.

The samples with the best results in dye adsorption were subjected to metal adsorption tests and surface characterization by nitrogen adsorption (BET), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Table 1. Contact time and concentration of HNO_3 and NH_4OH solutions for SMACs.

Sample	Time (h)	Concentration (%)*
1A (NH_4OH)	3:29	23.2%
5A (NH_4OH)	9:30	10.0%
7N (HNO_3)	1:00	55.0%
10N (HNO_3)	18:00	55.0%

* Percentage of the concentrated reagent diluted in distilled water

3. Results and Discussion

The modifications of commercial activated carbon (CAC) with NH_4OH and HNO_3 demonstrated varied impacts on their adsorption properties. SEM analysis provided insights into the morphological changes induced by the modifications, while EDS revealed the elemental composition of the surface related to possible functional groups. BET analysis quantified the surface area and porosity alterations. These physical changes are correlated with the observed improvements in dye and heavy metal adsorption.

Characterization

According to the surface analysis (BET) (Table 2), the sample with the largest surface area is the 1A SMAC. Samples 1A and 5A were those that had the greatest increase in mesopore volume (V_{BJH}), while samples 7N and 10N in general had slight reductions in their surface areas and pore volumes.

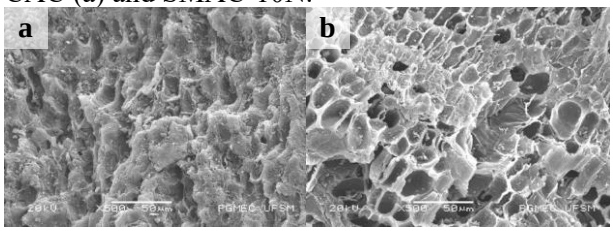
Table 2. Surface characteristics of the synthesized SMAC and CAC.

Sample	S_{BET}[a]	V_{tot}[b]	V_{mic}[c]	V_{BJH}[d]	D_{med}[e]
CAC	547.21	0.340	0.255	0.0484	2.010
1A	546.16	0.342	0.254	0.0516	2.013
5A	538.31	0.339	0.251	0.0499	2.017
7N	510.34	0.317	0.238	0.0447	2.015
10N	517.84	0.325	0.240	0.0465	2.012

a Surface area ($m^2 \cdot g^{-1}$)
b Total pore volume ($cm^3 \cdot g^{-1}$)
c Micropore volume, t-Plot method ($cm^3 \cdot g^{-1}$)
d BJH volume (desorption) ($cm^3 \cdot g^{-1}$)
e Average pore diameter (desorption) (nm)

SEM analyzes (Figure 1) show chemical attack on the CAC surface, causing changes in its texture.

Figure 1. SEM images at 500x magnification for the CAC (a) and SMAC-10N.



The results obtained by EDS (Table 3) demonstrate an increase in the content of oxygen atoms on the coal surface, after the modification processes, with this increase having a greater magnitude in reactions carried out with nitric acid (7N and 10N).

Table 3. EDS analyzes showing the elemental chemical composition of each AC sample.

AC	C		O		N	
	% (Atom)	SD (%)	% (Atom)	SD (%)	% (Atom)	SD (%)
CAC	90.86	9.89	5.87	1.37	2.97	1.01
1A	90.54	9.84	6.35	1.44	2.73	0.95
5A	90.13	9.90	7.17	1.66	2.70	1.01
7N	87.25	9.55	8.86	1.94	3.63	1.21
10N	88.99	9.58	8.27	1.72	2.75	0.91

Adsorption tests

For the tests with MB, the SMACs modified in an acidic medium obtained higher adsorption value compared to those modified in a basic medium and the CAC. The opposite occurs for tests with MO.

Table 4. Adsorption capacities ($mg \cdot g^{-1}$) of the four SMAC and CAC, for solutions of MB ($250\ mg \cdot L^{-1}$) and MO ($50\ mg \cdot L^{-1}$).

Sample	Amount of MB adsorbed ($mg \cdot g^{-1}$)	Amount of MO adsorbed ($mg \cdot g^{-1}$)
CAC	48.20	7.77
1A	47.17	8.18
5A	41.42	8.92
7N	47.72	9.85
10N	49.60	9.11

It is expected that activated carbons treated with base will present more positive charges on the surface, in an aqueous medium with approximately neutral pH, while coals treated with acid will present negative charges under the same conditions [3,6]. Therefore, SMAC 7N and 10N have greater affinity with cationic molecules, such as MB.

Adsorption tests with metal ions were performed to evaluate the capacity of the SMAC to remove small inorganic compounds from water, in addition to dyes, which serve as probes for organic compounds.

Table 5. Comparison between the adsorption capacities ($mg \cdot g^{-1}$) of the 4 SMAC and the the CAC, for solutions of Hg^{2+} $5\ mg \cdot L^{-1}$ (Mercury Chloride) ([a]) and Cr^{6+} $5\ mg \cdot L^{-1}$ (Potassium chromate) ([b])

Sample	Amount adsorbed[a] ($mg \cdot g^{-1}$)	Amount adsorbed[b] ($mg \cdot g^{-1}$)
CAC	0.800	0.132
1A	0.748	0.166
5A	0.774	0.199
7N	0.718	0.921
10N	0.849	0.928

For the mercury adsorption tests, only the 10N SMAC demonstrated better performance than the CAC, while for the chromate adsorption tests, the 7N and 10N carbons demonstrated much superior performance. This remarkable performance of samples treated with nitric acid for the removal of Cr^{6+} should be further investigated to verify the possibility that SMACs are promoting the reduction of Cr^{6+} para Cr^{3+}, altering the adsorption behavior [3,7].

Conclusion

The surface chemical modifications on the commercial activated carbon presented capabilities to change adsorption capacity and selectivity.

The surface chemical modification of CAC with NH_4OH and HNO_3 effectively enhances its adsorption capacities and selectivity, particularly for MO and Cr^{6+}. The HNO_3 modified carbons (7N and 10N) generally showed superior performance compared to NH_4OH modified samples and the unmodified CAC.

The obtained results make them promising candidates for treating water and wastewater contaminated with dyes and heavy metals. These findings contribute to the development of more efficient and versatile activated carbon adsorbents, addressing the need for improved water treatment technologies.

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